

Preliminary communication

Reactivity of carbon–metal bonds in organogold(I) complexes containing *o*-vinylphenyl and *o*-allylphenyl ligands

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We recently reported¹ that the Grignard reagent, prepared from *o*-chloroallylbenzene, reacts with anhydrous PtBr₂ or PtCl₂ in THF–C₆H₆ to give the complex *cis*-Pt(C₆H₄CH₂CH=CH₂-*o*)₂ (I) which is monomeric in benzene and contains the two double bonds coordinated to the metal. We have now prepared complexes from other metal halides in order to study the reactivity of the coordinated olefin.

The complex Ph₃PAuCl (II) (1 mole) reacts readily in toluene at room temperature with the Grignard reagent (1.1 moles) derived from *o*-bromostyrene or *o*-chloroallylbenzene, to give Ph₃PAu(C₆H₄CH=CH₂-*o*) (LAuBV, III) and Ph₃PAu(C₆H₄CH₂CH=CH₂) (LAuBA, IV) respectively, in nearly quantitative yields. The products are soluble in non polar solvents, insoluble in ethanol and pentane, and react with chlorinated solvents, the rate of reaction being CCl₄ > CHCl₃ > CH₂Cl₂ ≅ CH₂BrCl. The IR spectrum of (III) and (IV) (bands at 1615 and 1638 cm⁻¹, respectively) and proton magnetic resonances confirm that the double bonds are not coordinated to the metal.

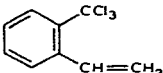
Treatment of (III) [or (IV)] with bromine (1 mole) in benzene at room temperature, gave Ph₃PAuBr (V) 90% and *o*-bromostyrene [or *o*-bromoallylbenzene] as a result of cleavage of the aryl–metal bonds². Similar reactions with III [or IV] performed in toluene at –40° gave insoluble yellow products which were stable for a limited period at –30° and which were characterized on the basis of elemental analysis and IR spectra, as gold(III) complexes of formula LAu(Br₂)BV and LAu(Br₂)BA respectively. Upon warming to room temperature, these solid products were converted into Ph₃PAuBr and *o*-bromostyrene (or *o*-bromoallylbenzene).

The phenyl–gold bonds in (III) or (IV) are also cleaved by anhydrous HCl (1/1 molar ratio) in benzene at room temperature, in contrast to Et₃PAuPh³, which is unaffected by HCl in EtOH–H₂O; but in agreement with Ph₃PAuPh, which reacts with concentrated HX (X = Cl, Br, I) in CHCl₃².

The reaction of (III) with CCl₄ in the absence of oxygen and moisture gave

TABLE I

Compound	Analysis: Found (calcd.)						m.p.
	C	H	Br	P	S		
$\text{Ph}_3\text{PAu}(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\cdot\text{o})$	56.1 (56.25)	4.0 (4.2)		5.40 (5.37)			123-125°
$\text{Ph}_3\text{PAu}(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\cdot\text{o})$	55.5 (55.52)	3.95 (3.94)		5.50 (5.51)			156-157°
$\text{Ph}_3\text{PAu}(\text{Br}_2)(\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2\cdot\text{o})$			22.1 (22.2)	4.31 (4.22)			Dec. from -20°
$\text{Ph}_3\text{PAu}(\text{SO}_2\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\cdot\text{o})$	49.5 (49.8)	3.75 (3.54)		4.88 (4.94)	5.18 (5.13)		117-119°
$\text{Ph}_3\text{PAu}(\text{Br}_2)(\text{SO}_2\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\cdot\text{o})$			21.2 (21.8)	4.09 (4.1)	4.16 (4.05)		Dec. from -20°

Ph_3PAuCl and  (VI) as an intermediate, which undergoes further reaction

depending upon the reaction conditions. In the presence of moist air (VI) could not be detected, but other products, at present under investigation were isolated. Both (III) and (IV) react with SO_2 at 0° to give the second example of an SO_2 insertion into the gold-carbon bond⁴. We formulate the products as *S*-sulphinato complexes on the bases of their IR spectra [bands at 1205 s and 1180 s cm^{-1} $\nu_{\text{asym}}(\text{SO}_2)$, and 1122 m and 1070 s cm^{-1} $\nu_{\text{sym}}(\text{SO}_2)$]; compare lower values for an *O*-sulphinato complex of $\nu_{\text{asym}}(\text{SO}_2)$ and $\nu_{\text{sym}}(\text{SO}_2)$ ⁵, usually in the region 1100–850 cm^{-1} .

The NMR spectrum shows that the allyl and vinyl groups are unaffected, but there is a slight shift in the olefin proton resonance which can be ascribed to the influence of the SO_2 moiety. The $\text{LAu}(\text{SO}_2\text{BV})$ *S*-sulphinato complex is more stable than the parent complex towards HCl, but it reacts with Br_2 at -60° to give a complex of formula $\text{Ph}_3\text{PAu}(\text{Br}_2)(\text{SO}_2\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)$ (VII) which decomposes above -20° to give Ph_3PAuBr together with an organic compound which does not apparently contain an olefinic bond. We believe that ring closure takes place between the olefin and the SO_2 group to give a sulphone.

(III) reacts with a suspension of PtCl_2 in benzene at room temperature to yield Ph_3PAuCl and $\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2)_2$ ¹, identified by its IR and NMR spectrum, m.p. and elemental analysis (Table 1). This provides the first example of transfer of a phenyl group from gold to a metal other than mercury^{2,6}.

We are extending the transfer reaction to those metal halides for which complexes analogous to (I) cannot be obtained directly from the Grignard reagent. Initial results show that this transfer is effective for PdCl_2 .

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