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Preliminary communication

ETHYNYLGOLD(I) COMPLEXES

RONALD J. CROSS*, MICHAEL F. DAVIDSON and ALISTAIR J. McLENNAN
Chemistry Department, The University, Glasgow G12 8QQ (Great Britain)

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Summary

Reactions between R_3PAuCl, NaOEt, and $HC{\equiv}CR'$ under mild conditions produce $R_3PAuC{\equiv}CR'$ in excellent yield. When $R' = H$, a second step leading to the formation of $R_3PAuC{\equiv}CAuPR_3$ can take place. Exchange reactions of ethynyl for chloride between the ethynylgold complexes and $HgCl_2$, *cis*-$[PtCl_2L_2]$, *cis*-$[PtCl_2(CO)L]$, and R'_3PAuCl have been monitored, revealing $R_3PAuC{\equiv}CR'$ to be useful alkynylating agents. In the reaction with *cis*-$[PtCl_2(CO)L]$, the first substitution step is non-specific.

Ethynylgold(I) complexes, $R_3PAuC{\equiv}CR'$, have previously been made either by the action of R_3P on polymeric $(AuC{\equiv}CR')_n$, or by treatment of R_3PAuCl by Grignard or organolithium reagents [1]. We report here a versatile and simple synthesis under mild conditions which exploits the acidity of terminal alkynes.

Treatment of ethanolic suspensions of Ph_3PAuCl by sodium ethoxide and the alkyne (bubbled through or added as liquid) at room temperature or 0°C led to dissolution of the starting complex followed by crystallisation of the ethynylgold complex (eq. 1, R = H, Me, Et, CF_3 or Ph).

$$Ph_3PAuCl + HC{\equiv}CR + NaOEt \xrightarrow{EtOH} Ph_3PAuC{\equiv}CR + NaCl \qquad (1)$$

In most cases, the product was obtained pure and in high yield simply by filtration. In the case of R = H, the product could be further treated with Ph_3PAuCl and NaOEt to produce $Ph_3PAuC{\equiv}CAuPPh_3$. With the more soluble starting complex $(p\text{-tol})_3PAuCl$, however, the reaction with C_2H_2 proceeded directly to the digold species in one step (equation 2).

$$2(p\text{-tol})_3PAuCl + C_2H_2 \xrightarrow[EtOH]{NaOEt} (p\text{-tol})_3PAuC{\equiv}CAuP(p\text{-tol})_3 \qquad (2)$$

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The only simple ethynyl-bridged digold complexes previously described are anionic species, $[RAuC\equiv CAuR]^{2-}$, prepared from gold carbide, $(Au_2C_2)_n$ [2].

A number of ethynylplatinum complexes have been made by related reactions, Et_2NH being employed both as solvent and base [3,4], and using CuI as a catalyst (eq. 3, L is tertiary phosphine).

$$[PtCl_2L_2] + 2HC\equiv CR \xrightarrow[CuI]{Et_2NH} [Pt(C\equiv CR)_2L_2] \qquad (3)$$

We have found that the use of Et_2NH as base and solvent in the reactions between Ph_3PAuCl and $HC\equiv CPh$ gave only partial reaction under conditions comparable to the ethoxide/ethanol route, thus the latter method seems preferable for ethynylgold syntheses. Its versatility was further illustrated by its use to synthesise a (known [5]) cyclopentadienylgold complex.

$$Ph_3PAuCl + C_5H_6 \xrightarrow[EtOH]{NaOEt} Ph_3PAuC_5H_5 \qquad (4)$$

The ethynyl groups from the gold complexes can readily be exchanged for chloride from several other metal atoms. With $HgCl_2$ and *cis*-$[PtCl_2L_2]$ (L = $PMePh_2$), both halides are readily replaced by ethynyl from gold (eq. 5 and 6, respectively).

$$2Ph_3PAuC\equiv CPh + HgCl_2 \rightarrow 2Ph_3PAuCl + Hg(C\equiv CPh)_2 \qquad (5)$$

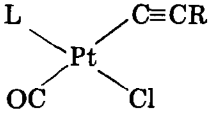
$$2Ph_3PAu(C\equiv CPh) + [PtCl_2L_2] \rightarrow 2Ph_3PAuCl + [Pt(C\equiv CPh)_2L_2] \qquad (6)$$

Since ethynylmercury compounds readily transfer their organic groups to platinum in reactions of this type [6], the ethynyl transfer sequence in these exchange reactions is established as $Au^{I} > Hg^{II} > Pt^{II}$.

Both chloride ions of *cis*-$[PtCl_2(CO)L]$ (L = $PMePh_2$) are also replaced by ethynyl from $Ph_3PAuC\equiv CR$ (R = Me or Ph).

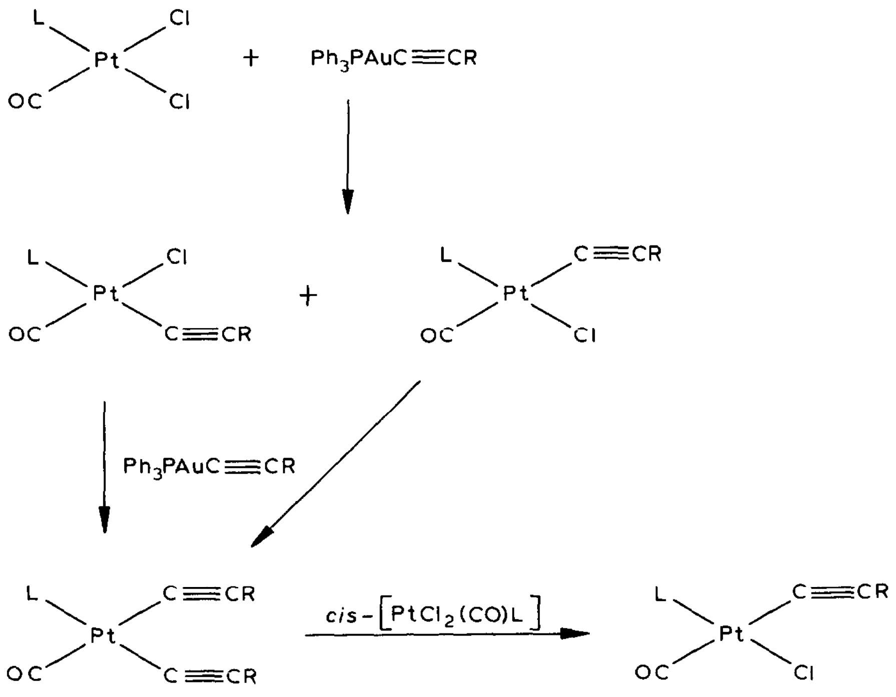
$$2Ph_3PAuC\equiv CR + cis\text{-}[PtCl_2(CO)L] \rightarrow 2Ph_3PAuCl + cis\text{-}[Pt(C\equiv CR)_2(CO)L] \qquad (7)$$

The 1/1 reaction appears to be simple and specific (eq. 8) leading to one isomer only of the product.

$Ph_3PAuC\equiv CR$ + *cis*-$[PtCl_2(CO)L]$ →  + Ph_3PAuCl (8)

When monitored at low temperature by ^{31}P NMR spectroscopy, however, it is apparent that several reactions are involved. Unlike related transfers from organomercurials [6,7], the first replacement step at platinum is not stereospecific. Moreover, both of the isomers produced then react with more $Ph_3PAuC\equiv CR$, competing successfully with unreacted $[PtCl_2(CO)L]$. The final step is the known [6] reaction between *cis*-$[PtCl_2(CO)L]$ and *cis*-$[Pt(C\equiv CR)_2(CO)L]$. The scheme summarises these reactions.

Finally, equilibria are rapidly established between ethynylgold and gold halide complexes (eq. 9).



SCHEME 1

$$Ph_3PAuC{\equiv}CPh + (p\text{-tol})_3PAuCl \rightleftharpoons Ph_3PAuCl + (p\text{-tol})_3PAuC{\equiv}CPh \qquad (9)$$

Whilst we can not at this stage rule out phosphine exchange as being responsible, analogy with the other reactions would suggest that this, too, is an exchange of ethynyl for chloride.

The general and easy syntheses of the ethynylgold complexes, and the ease with which they transfer their ethynyls to other metals, indicate that they can be developed as useful synthetic reagents. Further work is in progress to evaluate their potential.

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