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Preliminary communication

THE REACTIVITY OF THE BIS(PHENYLETHYNYL)AURATE(I) COMPLEX ANION. SYNTHESIS AND CHARACTERIZATION OF NOVEL DI- AND TRI-NUCLEAR GROUP IB METAL ARYLACETYLIDES

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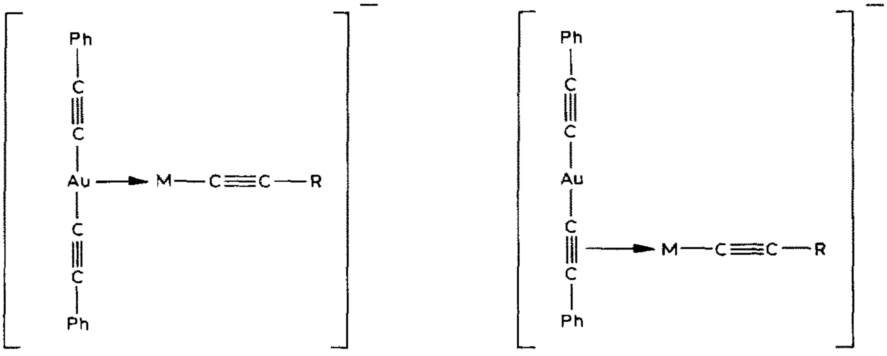
Summary

The syntheses of the novel complexes $((PPh_3)_2N)(PhC_2AuC_2Ph)(MC_2R)$ (I: M = Au, R = Ph; II: M = Ag, R = p-MeC_6H_4) and $((PPh_3)_2N)(PhC_2AuC_2Ph)$-$(AuC_2Ph)(CuC_2$-$p$-$MeC_6H_4)$ (III) are described and structures considered.

It was recently reported that the diorganocuprate(I) complex anion $(PhC_2CuC_2Ph)^-$ is a useful ethynylating agent [1]. For example, it depolymerises gold phenylacetylide, $(AuC_2Ph)_n$, to give the analogous gold(I) complex anion $(PhC_2AuC_2Ph)^-$. It was also found that the anions Cl^-, Br^-, or I^- readily displace the π-bond in $(AuC_2Ph)_n$ to give the organogold(I) halide complex anions $(XAuC_2Ph)^-$ (X = Cl, Br, I) [2]. We have now found that the bis(phenylethynyl)aurate(I) complex anion depolymerises both gold and silver arylacetylides, affording the novel 1/1 adducts $((PPh_3)_2N)(PhC_2AuC_2Ph)$-$(MC_2R)$ (I: M = Au, R = Ph; II: M = Ag, R = p-MeC_6H_4). The synthesis of an even more interesting trinuclear complex $((PPh_3)_2N)(PhC_2AuC_2Ph)(AuC_2Ph)$-$(CuC_2$-$p$-$MeC_6H_4)$ (III) from the reaction of complex I and excess copper(I) p-tolylacetylide has also been carried out.

Slow addition (2/1) of gold phenylacetylide to a solution of $((PPh_3)_2N)$-(PhC_2AuC_2Ph) in acetone at room temperature produces a yellow solution and a yellowish pale green residue. From the solution the 1/1 adduct $((PPh_3)_2N)(PhC_2AuC_2Ph)(AuC_2Ph)$ (I) may be obtained in high yield after repeated crystallization. The analytical data for the product indicate that it is a structural isomer of gold phenylacetylide. It has two sharp $\nu(C\equiv C)$ bands at ca. 2030 and 1985 cm^{-1} in contrast to the well-known linear isomer $(AuC_2Ph)_n$, which has a very weak $\nu(C\equiv C)$ band at ca. 1970 cm^{-1} [3].

The molecular formula of complex I, which is a stable off-white solid, was deduced from full analytical data and molecular weight determination. Thus by vaporimetric methods give the molecular weight expected for a 1/1 electrolyte (found M = 665; calcd. M = 1235). The IR spectrum contained a medium band at ca. 2110 cm^{-1} characteristic of σ-acetylides. Structure A is favoured over structure B because of (a) the absence of a clear $\nu(C\equiv C)$ band in 1900—2000 cm^{-1} region characteristic of gold acetylide η-type bonds, and (b) the fact that diphenylacetylene does not react with $[AuC_2Ph]_n$ [3].



(A) (B)

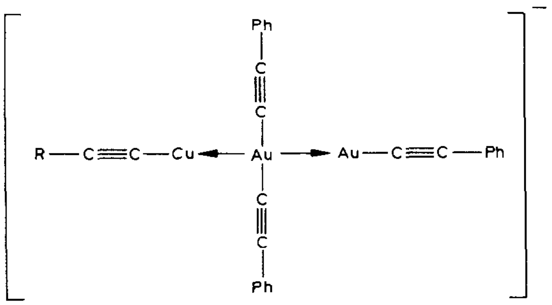
(I M = Au, R = Ph; II M = Ag, R = $p\text{-MeC}_6\text{H}_4$)

The main feature of structure A is the dative bond between gold atoms, with no change in the geometry of the two alkynyl groups about the donor gold atom. The geometry about the other gold atom is also linear. X-ray structural studies recently revealed that the chain polymer of stoichiometry $(Au(C_6F_5)_2AgSC_4H_8)$ has gold—silver metal bonds; the geometry of the two pentafluorophenyl groups about the donor gold atom scarcely deviates from linearity [4].

In a similar reaction, silver p-tolylacetylide dissolves completely when added (1/1) to a solution of $((PPh_3)_2N)(PhC_2AuC_2Ph)$ in acetone. The data obtained for the product indicate a 1/1 adduct $((PPh_3)_2N)(PhC_2AuC_2Ph)(AgC_2\text{-}p\text{-}MeC_6H_4)$ (II). The IR spectrum for this complex has a $\nu(C\equiv C)$ band at 2105 cm^{-1}. This complex probably has a similar structure to that of complex I.

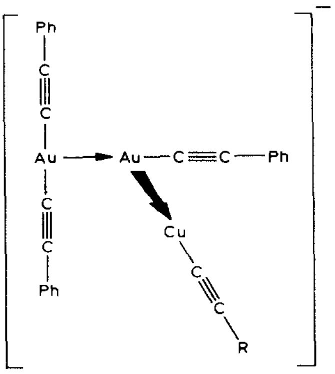
Copper p-tolylacetylide does not react with the bis(phenylethynyl)aurate(I) complex but when excess of the copper complex is added to complex I in acetone, it partly dissolves. The trinuclear complex $((PPh_3)_2N)(PhC_2AuC_2Ph)(AuC_2Ph)(CuC_2\text{-}p\text{-}MeC_6H_4)$ (III), a stable yellow solid, is obtained in moderate yields. Full analytical data for complex III indicate that it is a 1/1 adduct, and molecular weight determination indicates that it is a 1/1 electrolyte (Found M = 854; calcd. M = 1413.5). The IR spectrum shows two $\nu(C\equiv C)$ bands at ca. 2110 and 2070 cm^{-1}. Possible structures for this novel complex are C and D.

It is not clear at this stage why the bis(phenylethynyl)aurate(I) complex anion does not react with the copper complex, while complex I does. Cur-



(C)

(Complex III ; R = p-MeC$_6$H$_4$)



(D)

rent investigations indicate that complexes I and II are potentially useful precursors for polynuclear arylacetylides and, in theory at least, it is possible under the right conditions to control addition of one or more molecules of group IB Metal arylacetylides.

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