

Preliminary communication

ETHYNYLATION REACTIONS USING THE BIS(PHENYLETHYNYL)-CUPRATE(I) COMPLEX ANION. PREPARATION OF THE BIS(PHENYLETHYNYL)AURATE(I) COMPLEX ANION

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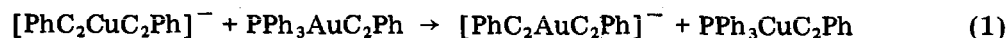
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Summary

Four new routes are described for the preparation of the linear diorganocuprate(I) complex $[\text{PhC}_2\text{AuC}_2\text{Ph}]^-$. These are based on the reactions of the analogous copper(I) complex anion $[\text{PhC}_2\text{CuC}_2\text{Ph}]^-$ with $[\text{PPh}_3\text{AuC}_2\text{Ph}]$, $[\text{PPh}_3\text{AuCl}]$, $[\text{ClAuC}_2\text{Ph}]^-$, or $[\text{AuC}_2\text{Ph}]_n$.

Copper(I) and silver(I) arylacetylides produced fascinating organometallic complexes when treated with coordinatively-unsaturated complexes [1]. In our investigations of the reactivity of the diorganocuprate(I) complex $[\text{PhC}_2\text{CuC}_2\text{Ph}]^-$, which was originally prepared as its sodium and potassium salts by Nast et al. [2], we found that the complex is very useful in organometallic synthesis. For example, it acts as an ethynylating agent when treated with the gold complexes $[\text{PPh}_3\text{AuC}_2\text{Ph}]$, $[\text{PPh}_3\text{AuCl}]$, $[\text{ClAuC}_2\text{Ph}]^-$ or $[\text{AuC}_2\text{Ph}]_n$.

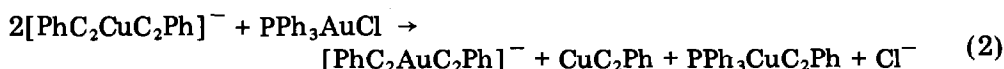
Thus the reaction of the complex $[(\text{PPh}_3)_2\text{N}][\text{PhC}_2\text{CuC}_2\text{Ph}]$, which is notably stabler than the sodium or potassium salts, with $[\text{PPh}_3\text{AuC}_2\text{Ph}]$ at room temperature in dichloromethane proceeded smoothly according to eq. 1.



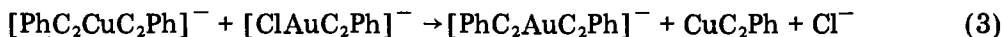
The gold complex anion was obtained in a very high yield (ca. 95%) and was characterised by the usual methods and comparison with the data published for the complex $[\text{PPh}_4][\text{PhC}_2\text{AuC}_2\text{Ph}]$ [3]. The $\nu(\text{C}\equiv\text{C})$ band for the gold complex anion occurs at ca. 2105 cm^{-1} . This frequency is higher by ca. 25 cm^{-1} than that for the copper(I) analogue, but is lower by ca. 20 cm^{-1} than that of the complex $[\text{PPh}_3\text{AuC}_2\text{Ph}]$. The other product of the above reaction, $\text{PPh}_3\text{CuC}_2\text{Ph}$, was also obtained in a high yield, and characterized by the usual methods [4]. Previously the gold complex anion $[\text{PhC}_2\text{AuC}_2\text{Ph}]^-$ has been prepared either by the reaction of AuI with KC_2Ph (1/2) or of AuC_2Ph with KC_2Ph (1/1) in liquid

ammonia [3,5]. Other linear diorganoaurate(I) complexes were prepared using lithium reagents at low temperatures [6]. Apparently the lower tendency of copper(I) than gold(I) towards linear geometry [7] helps to drive this reaction, since tertiary phosphine complexes of copper phenylacetylide are dimeric in nitrobenzene solution, and, therefore, are not linear [4]. Tertiary phosphine complexes of alkylgold(I) complexes [8] are markedly more thermally stable than tertiary phosphine complexes of alkylcopper(I) complexes [9] and so the relative strength of the carbon-gold σ -bond may also contribute to the driving force for this reaction.

Both ligands in the complex $[\text{PPh}_3\text{AuCl}]$ were displaced by phenylethynyl groups when it was added slowly (1/2) to a solution of $[\text{PhC}_2\text{CuC}_2\text{Ph}]^-$ in dichloromethane, $[\text{CuC}_2\text{Ph}]_n$ also being obtained (eq. 2).



The organogold(I) chloride complex $[\text{ClAuC}_2\text{Ph}]^-$, which we reported recently [10], produced the same diorganogold(I) complex anion in a high yield when added (1/1) to a dichloromethane solution of the same copper(I) complex anion. Copper(I) phenylacetylide was the other product (eq. 3).



It was recently shown that the organogold(I) iodide complex anion $[\text{IAuC}_2\text{Ph}]^-$ gives the same diorganogold(I) complex anion when treated (1/1) with PPh_3 [10].

Finally, the same diorganogold(I) complex was obtained by the reaction (1/1) of the copper reagent with phenylethynylgold, $[\text{PhC}_2\text{Au}]_n$. Phenylethynylcopper was the other product (eq. 4).



In this reaction the phenylacetylide group replaced the π -bond in $[\text{AuC}_2\text{Ph}]_n$.

In all the above reactions the gold retained its linear geometry while copper lost its linear geometry.

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