Journal of Organometallic Chemistry, 255 (1983) C39—C40
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

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

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(Received July 12th, 1983)

Summary

Four new routes are described for the preparation of the linear diorgano-aurate(I) complex $[PhC_2AuC_2Ph]^-$. These are based on the reactions of the analogous copper(I) complex anion $[PhC_2CuC_2Ph]^-$ with $[PPh_3AuC_2Ph]$, $[PPh_3AuCl]$, $[ClAuC_2Ph]^-$, or $[AuC_2Ph]_n$.

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 $[PhC_2CuC_2Ph]^-$, 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 $[PPh_3AuC_2Ph]$, $[PPh_3AuCl]$, $[ClAuC_2Ph]^-$ or $[AuC_2Ph]_n$.

Thus the reaction of the complex $[(PPh_3)_2N][PhC_2CuC_2Ph]$, which is notably stabler than the sodium or potassium salts, with $[PPh_3AuC_2Ph]$ at room temperature in dichloromethane proceeded smoothly according to eq. 1.

$$[PhC_2CuC_2Ph]^- + PPh_3AuC_2Ph \rightarrow [PhC_2AuC_2Ph]^- + PPh_3CuC_2Ph \qquad (1)$$

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 $[PPh_4][PhC_2AuC_2Ph]$ [3]. The $\nu(C{\equiv}C)$ 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 $[PPh_3AuC_2Ph]$. The other product of the above reaction, PPh_3CuC_2Ph, was also obtained in a high yield, and characterized by the usual methods [4]. Previously the gold complex anion $[PhC_2AuC_2Ph]^-$ 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 $[\mathrm{PPh_3AuCl}]$ were displaced by phenylethynyl groups when it was added slowly (1/2) to a solution of $[\mathrm{PhC_2CuC_2Ph}]^-$ in dichloromethane, $[\mathrm{CuC_2Ph}]_n$ also being obtained (eq. 2).

$$2[\mathrm{PhC_2CuC_2Ph}]^- + \mathrm{PPh_3AuCl} \rightarrow [\mathrm{PhC_2AuC_2Ph}]^- + \mathrm{CuC_2Ph} + \mathrm{PPh_3CuC_2Ph} + \mathrm{Cl}^- \qquad (2)$$

The organogold(I) chloride complex $[\mathrm{ClAuC_2Ph}]^-$, 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).

$$[\mathrm{PhC_2CuC_2Ph}]^- + [\mathrm{ClAuC_2Ph}]^- \rightarrow [\mathrm{PhC_2AuC_2Ph}]^- + \mathrm{CuC_2Ph} + \mathrm{Cl}^- \qquad (3)$$

It was recently shown that the organogold(I) iodide complex anion $[\mathrm{IAuC_2Ph}]^-$ gives the same diorganogold(I) complex anion when treated (1/1) with $\mathrm{PPh_3}$ [10].

Finally, the same diorganogold(I) complex was obtained by the reaction (1/1) of the copper reagent with phenylethynylgold, $[\mathrm{PhC_2Au}]_n$. Phenylethynylcopper was the other product (eq. 4).

$$[\mathrm{PhC_2CuC_2Ph}]^- + \mathrm{AuC_2Ph} \rightarrow [\mathrm{PhC_2AuC_2Ph}]^- + \mathrm{CuC_2Ph} \qquad (4)$$

In this reaction the phenylacetylide group replaced the π-bond in $[\mathrm{AuC_2Ph}]_n$.

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

Acknowledgements. We thank Mr. M.K. Mahmoud and Mr. M. Ja'far for technical assistance.

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