Preparation and Reactivity of Bis(phenylethynyl)argentate(I) and Chlorophenylethynylargentate(I) Complex Anions

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It has been reported recently that bis(phenylethynyl)cuprate(I) complex anion $[PhC_2CuC_2Ph]^-$ is a useful ethynylating agent for some gold(I) complexes, where a phenylethynyl ligand displaces a chloride, a π-bond or a tertiary phosphine [1]. We report in this letter the preparation of two silver(I) complex anions $[PPN][PhC_2AgC_2Ph]$ (I) and $[PPN][ClAgC_2Ph]$ (II) and their behaviour as ethynylating agents towards some gold(I) and platinum(II) complexes. Both complexes were mentioned very briefly in a ^{13}C NMR study for some alkynyl complexes [2]. Complex **I** is best prepared in very high yield by reacting $[(PPh_3)_2N][Cl]$, $[AgC_2Ph]_n$, and PPh_3 in 1:2:3 mole ratio in acetone at room temperature (eqn. (1)).

$$[PPN][Cl] + 2AgC_2Ph + 3PPh_3 \longrightarrow [PPN][PhC_2AgC_2Ph] + (Ph_3P)_3AgCl \quad (1)$$

Both products were characterized by the usual methods. Complex **I** has a $\nu(C{\equiv}C)$ band at *ca.* 2085 cm^{-1} which is lower by *ca.* 15–20 cm^{-1} than that of the gold(I) analogue [1, 3]. It is markedly more stable than the analogous potassium salt described earlier [4] towards moisture and light. It is believed that Ph_3P attacks the chloride derivative $[ClAgC_2Ph]^-$ formed during the reaction (*vide infra*).

Complex **I** reacts with Ph_3PAuCl and *cis*-$(Ph_3P)_2PtCl_2$ where both phenylethynyl ligands are exchanged. Thus the reaction of Ph_3PAuCl with complex **I** in acetone at room temperature results in immediate precipitation of $[Ph_3PAgCl]_4$. Complex **I** is obtained by dissolving the residue, obtained by evaporating the filtrate, in dichloromethane followed by addition of hexane (eqn. (2)).

$$[PhC_2AgC_2Ph]^- + Ph_3PAuCl \longrightarrow [PhC_2AuC_2Ph]^- + Ph_3PAgCl \quad (2)$$

Both products were identified by the usual methods [1, 5]. When *cis*-$(Ph_3P)_2PtCl_2$ was employed, the major product was the *cis*-isomer $(Ph_3P)_2Pt(C_2Ph)_2$ (*ca.* 80%) with a small quantity of the *trans* isomer (*ca.* 6%) [6]. The silver(I) complex [PPN][ClAgCl] was obtained as the second product of this reaction also in very high yield (eqn. (3)).

$$[PhC_2AgC_2Ph]^- + (Ph_3P)_2PtCl_2 \longrightarrow (Ph_3P)_2Pt(C_2Ph)_2 + [ClAgCl]^- \quad (3)$$

It is of interest to report that the reaction of the analogous copper(I) complex with the same platinum reagent requires a 2:1 mole ratio of the reactants for complete displacement of the chloride (eqn. (4)).

$$2[PhC_2CuC_2Ph]^- + (Ph_3P)_2PtCl_2 \longrightarrow (Ph_3P)_2Pt(C_2Ph)_2 + 2CuC_2Ph + 2Cl^- \quad (4)$$

The chlorophenylethynylargentate(I) complex anion $[PPN][ClAgC_2Ph]$ (II) was prepared in very high yield by addition of chloride ions to silver phenylacetylide in acetone in a way similar to that employed for the analogous gold(I) complex mentioned elsewhere [7]. It was characterised by the usual methods. It has a $\nu(C{\equiv}C)$ band at 2090 cm^{-1}. This complex is the first organosilver(I) derivative which is simultaneously σ-bonded to carbon and halogen to be reported. It reacts with excess Ph_3P giving complex **I** in very high yield (eqn. (5))

$$2[ClAgC_2Ph]^- + 3Ph_3P \longrightarrow [PhC_2AgC_2Ph]^- + (Ph_3P)_3AgCl + Cl^- \quad (5)$$

A similar reaction between $[IAuC_2Ph]^-$ and Ph_3P was reported recently [7]. Complex **II** is also an ethynylating agent. With Ph_3PAuC_2Ph, the following reaction takes place (eqn. (6))

$$Ph_3PAuC_2Ph + [ClAgC_2Ph]^- \longrightarrow [PhC_2AuC_2Ph]^- + Ph_3PAgCl \quad (6)$$

The same platinum(II) complex mentioned above requires a two-fold excess of complex **II** (eqn. (7))

$$(Ph_3P)_2PtCl_2 + 2[ClAgC_2Ph]^- \longrightarrow (Ph_3P)_2Pt(C_2Ph)_2 + 2[ClAgCl]^- \quad (7)$$

The latter reaction is less specific than the silver–platinum reaction.

In the reactions of complex **I**, it is likely that complex **II** is formed from the chloride exchanged and AgC_2Ph produced. Complex **II**, once formed, exchanges its phenylethynyl ligand. This results in displacement of both ligands attached to gold atom or both chloride ions in the case of platinum(II) complex. This probably also explains the high specificity of the reaction between complex **I** and *cis*-(Ph$_3$-

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$P)_2PtCl_2$. In the reactions between $[PhC_2CuC_2Ph]^-$ and both gold(I) and platinum(II) complexes, the chloride displaced does not react with CuC_2Ph produced, which may account for the difference in behaviour of copper(I) and silver(I) analogues as ethynylating agents in these reactions.

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