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TRIPHENYLPHOSPHINE COMPLEXES OF Cu(I), Ag(I) AND Au(I) N,N-DIALKYLTHIOCARBAMATES.

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The synthesis and properties of bis-triphenylphosphine complexes of Cu(I) and Ag(I) N,N-dialkyldithiocarbamates \( \left[ \text{(Ph}_3\text{P)}_2\text{M(R}_2\text{dtc)} \right] \) were reported by Kowala and Swan (1). Molecular weights of these compounds in benzene or chloroform were 30 - 50% lower than the calculated values. In spite of the low conductivities in chloroform and nitrobenzene solutions Kowala and Swan suggested that these complexes are best formulated as \( \text{(Ph}_3\text{P)}_2\text{M}^{+}\text{.R}_2\text{dtc}^- \). We have reinvestigated the \( \text{Et}_2\text{dtc} \) complexes, and have also succeeded in preparing \( \text{(Ph}_3\text{P)}_2\text{Au(Et}_2\text{dtc)} \). Conductivity studies in nitrobenzene show the Cu, Ag and Au complexes to be non-electrolytes (at a concentration of 10^-2 mole/l the molar conductivity is lower than 0.1 ohm^-1 cm^2 mole^-1). Osmometrically determined molecular weights are summarized in the TABLE. The combined results clearly indicate a dissociation:

\[
\text{(Ph}_3\text{P)}_2\text{M(R}_2\text{dtc)} \rightarrow \text{(Ph}_3\text{P)}\text{M(R}_2\text{dtc)} + \text{Ph}_3\text{P}
\]

It is noteworthy that the dissociation increases in the order Cu < Ag < Au. Our finding that the Au complex in benzene is completely dissociated, is confirmed by the synthesis of \( \text{(Ph}_3\text{P)}\text{Au(Et}_2\text{dtc)} \) which is monomeric in benzene solution (TABLE).

Attempts to prepare \( \text{(Ph}_3\text{P)}\text{M(Et}_2\text{dtc)} \) \( \text{M} = \text{Cu, Ag} \) were unsuccessful. In contrast with the report by Kowala and Swan addition of methyl iodide to a solution of the bisphosphine complexes in benzene results in the formation...
Molecular weight determinations were performed using the Hewlett Packard vapour pressure osmometer 302 B. 

\[(\text{Ph}^3\text{P})_2\text{M(} \text{Et}_2\text{dtc}) \ldots \text{M} = \text{Cu, Ag} \] were prepared as previously reported (1).

\[(\text{Ph}^3\text{P})_2\text{Au(} \text{Et}_2\text{dtc}) \] was prepared on addition of two moles \(\text{Ph}^3\text{P}\) to 1 mole \(\text{Au(} \text{Et}_2\text{dtc})\) (2) in acetone solution. Colourless needles were obtained, m.p. 134-136°.

Anal. Found: C, 56.4; H, 4.4; Au, 22.7. Calc. for \(\text{Ph}^3\text{P})_2\text{Au(} \text{Et}_2\text{dtc})\): C, 56.6; H, 4.6; Au, 22.6%.

\[(\text{Ph}^3\text{P})\text{Au(} \text{Et}_2\text{dtc}) \] was prepared by adding equivalent amounts of \(\text{Na(} \text{Et}_2\text{dtc})_2\text{H}_2\text{O}\) (Fluka A.G.) in ethanol to a solution of \(\text{Ph}^3\text{P})\text{AuCl}\) (3) in \(\text{CH}_2\text{Cl}_2\). \(\text{NaCl}\) was filtered off and, the solvent was evaporated under vacuo.

The residue was recrystallised from ethanol. Light yellow needles were obtained, m.p. 152 - 153°.

Anal. Found: C, 46.0; H, 4.1; N, 2.3; S, 10.5; Au, 32.4. Calc. for \(\text{Ph}^3\text{P})\text{Au(} \text{Et}_2\text{dtc})\): C, 45.5; H, 4.1; N, 2.3; S, 10.6; Au, 32.5%.

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