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

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The synthesis and properties of bis-triphenylphosphine complexes of Cu(I) and Ag(I) N,N-dialkyldithiocarbamates were reported by Kowala and Swan. 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 (Ph₃P)₂M(R₂dtc). We have reinvestigated the Et₂dtc complexes, and have also succeeded in preparing (Ph₃P)₂Au(Et₂dtc). 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 cm² mole⁻¹). Osmometrically determined molecular weights are summarized in the TABLE. The combined results clearly indicate a dissociation:

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

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 (Ph₃P)Au(Et₂dtc) which is monomeric in benzene solution (TABLE).

Attempts to prepare (Ph₃P)₂M(Et₂dtc) ... M = Cu, Ag were unsuccessful. In contrast with the report by Kowala and Swan addition of methyl iodide to a solution of the bis-phosphine complexes in benzene results in the formation of...
### Table

Molecular weights of \((\text{Ph}_3\text{P})_2\text{M}(\text{Et}_2\text{dtc})\) and \((\text{Ph}_3\text{P})\text{Au}(\text{Et}_2\text{dtc})\) in benzene at 37°.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Ph}_3\text{P})_2\text{Cu}(\text{Et}_2\text{dtc}))</td>
<td>600</td>
<td>736</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})_2\text{Ag}(\text{Et}_2\text{dtc}))</td>
<td>450</td>
<td>781</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})_2\text{Au}(\text{Et}_2\text{dtc}))</td>
<td>430</td>
<td>870</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})\text{Au}(\text{Et}_2\text{dtc}))</td>
<td>600</td>
<td>607</td>
</tr>
</tbody>
</table>

of methyltriphenylphosphonium iodide, supporting the idea of dissociation into free phosphine.

### Experimental

Molecular weight determinations were performed using the Hewlett Packard vapour pressure osmometer 302 B. \((\text{Ph}_3\text{P})_2\text{M}(\text{Et}_2\text{dtc})\) \(\ldots\) \(\text{M} = \text{Cu}, \text{Ag}\) 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 \(\text{Na}(\text{Et}_2\text{dtc})\cdot3\text{H}_2\text{O}\) (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 recrystallized 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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REFERENCES