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

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The synthesis and properties of bis-triphenylphosphine complexes of Cu(I) and Ag(I) N,N-dialkyldithiocarbamates \( [\text{Ph}_3\text{P}]_2\text{M}(\text{R}_2\text{dtc}) \) 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 \( (\text{Ph}_3\text{P})_2\text{M}^+.\text{R}_2\text{dtc}^- \). We have reinvestigated the \( \text{Et}_2\text{dtc} \) complexes, and have also succeeded in preparing \( (\text{Ph}_3\text{P})_2\text{Au}(\text{Et}_2\text{dtc}) \). 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:

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

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 \( (\text{Ph}_3\text{P})\text{Au}(\text{Et}_2\text{dtc}) \) which is monomeric in benzene solution (TABLE).

Attempts to prepare \( (\text{Ph}_3\text{P})\text{M}(\text{Et}_2\text{dtc}) \) \( \cdot \) \( \text{M} = \text{Cu}, \text{Ag} \) 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...
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 methyltriphosphonium 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 Na(\(\text{Et}_2\text{dtc})\).3\(\text{H}_2\text{O}\) (Fluka A.G.) in ethanol to a solution of \((\text{Ph}_3\text{P})\text{AuCl}\) (3) in \(\text{CH}_2\text{Cl}_2\). 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