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
\[(\text{Ph}_3\text{P})_2\text{M(Et}_2\text{dtc)}\] 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 \((\text{Ph}_3\text{P})_2\text{M}^+.\text{Et}_2\text{dtc}^-
\). We have reinvestigated the \text{Et}_2\text{dtc} complexes, and have
also succeeded in preparing \((\text{Ph}_3\text{P})_2\text{Au(}\text{Et}_2\text{dtc)}\). Conduct-

ivity 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:

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

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 \((\text{Ph}_3\text{P})\text{M(}\text{Et}_2\text{dtc)}\) \(\ldots M = \text{Cu, Ag}\) 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
TABLE

Molecular weights of \((\text{Ph}_3\text{P})_2\text{M(}	ext{Et}_2\text{dtc})\) and \((\text{Ph}_3\text{P})\text{Au(}	ext{Et}_2\text{dtc})\)
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(}	ext{Et}_2\text{dtc}))</td>
<td>600</td>
<td>736</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})_2\text{Ag(}	ext{Et}_2\text{dtc}))</td>
<td>450</td>
<td>781</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})_2\text{Au(}	ext{Et}_2\text{dtc}))</td>
<td>430</td>
<td>870</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})\text{Au(}	ext{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. \((\text{Ph}_3\text{P})_2\text{M(}	ext{Et}_2\text{dtc})\) \(\ldots\) \(\text{M} = \text{Cu, Ag}\) were prepared as previously reported (1). \((\text{Ph}_3\text{P})_2\text{Au(}	ext{Et}_2\text{dtc})\) was prepared on addition of two moles \(\text{Ph}_3\text{P}\) to 1 mole \(\text{Au(}	ext{Et}_2\text{dtc})\) (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 \((\text{Ph}_3\text{P})_2\text{Au(}	ext{Et}_2\text{dtc})\): C, 56.6; H, 4.6; Au, 22.6.

\((\text{Ph}_3\text{P})\text{Au(}	ext{Et}_2\text{dtc})\) was prepared by adding equivalent amounts of \(\text{Na(}	ext{Et}_2\text{dtc})\).\(\text{NaCl}\) (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 \((\text{Ph}_3\text{P})\text{Au(}	ext{Et}_2\text{dtc})\): C, 45.5; H, 4.1; N, 2.3; S, 10.6; Au, 32.5.

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REFERENCES