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

H.C. Brinkhoff, A.G. Matthijssen, C.G. Oomes
(Department of Inorganic Chemistry, University of Nijmegen,
Driehuizerweg 200, Nijmegen, The Netherlands).

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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 \((\text{Ph}_3\text{P})_2\text{Au}(\text{Et}_2\text{dtc})\). 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:

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

It is noteworthy that the dissociation increases in the
order Cu \(\prec\) Ag \(\prec\) 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 \((\text{Ph}_3\text{P})\text{M}(\text{Et}_2\text{dtc})\) ... \(\text{M} = \text{Cu}, \text{Ag}\) 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 \((\text{Ph}_3\text{P})_2\text{M(ET}_2\text{dtc})\) and \((\text{Ph}_3\text{P})\text{Au(ET}_2\text{dtc})\) 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(ET}_2\text{dtc}))</td>
<td>600</td>
<td>736</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})_2\text{Ag(ET}_2\text{dtc}))</td>
<td>450</td>
<td>781</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})_2\text{Au(ET}_2\text{dtc}))</td>
<td>430</td>
<td>870</td>
</tr>
<tr>
<td>((\text{Ph}_3\text{P})\text{Au(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 102 B.

\((\text{Ph}_3\text{P})_2\text{M(ET}_2\text{dtc})\) \(\text{M} = \text{Cu, Ag}\) were prepared as previously reported (1).

\((\text{Ph}_3\text{P})_2\text{Au(ET}_2\text{dtc})\) was prepared on addition of two moles \text{Ph}_3\text{P} to 1 mole \text{Au(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 \((\text{Ph}_3\text{P})_2\text{Au(ET}_2\text{dtc})\): C, 56.6; H, 4.6; Au, 22.6%

\((\text{Ph}_3\text{P})\text{Au(ET}_2\text{dtc})\) was prepared by adding equivalent amounts of Na(ET_2dtc).3H_2O (Fluka A.G.) in ethanol to a solution of \((\text{Ph}_3\text{P})\text{AuCl}\) (3) in CH_2Cl_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 \((\text{Ph}_3\text{P})\text{Au(ET}_2\text{dtc})\): C, 45.5; H, 4.1; N, 2.3; S, 10.6; Au, 32.5%

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REFERENCES