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

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-dialkylthiolcarbamates \([\text{Ph}_3\text{P}]_2\text{M(Ph}_2\text{dtc)}\) 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 \((\text{Ph}_3\text{P})_2\text{M}^+\text{R}_2\text{dtc}^-\). 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:

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

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 \((\text{Ph}_3\text{P})\text{Au(Ph}_2\text{dtc)}\) 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
TABLE

Molecular weights of (Ph₃P)ₓM(Et₂dtc) and (Ph₃P)Au(Et₂dtc) in benzene at 37°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ph₃P)ₓCu(Et₂dtc)</td>
<td>600</td>
<td>736</td>
</tr>
<tr>
<td>(Ph₃P)ₓAg(Et₂dtc)</td>
<td>450</td>
<td>781</td>
</tr>
<tr>
<td>(Ph₃P)ₓAu(Et₂dtc)</td>
<td>430</td>
<td>870</td>
</tr>
<tr>
<td>(Ph₃P)Au(Et₂dtc)</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. (Ph₃P)ₓM(Et₂dtc) ... M = Cu, Ag were prepared as previously reported (1).

(Ph₃P)ₓAu(Et₂dtc) was prepared on addition of two moles Ph₃P to 1 mole Au(Et₂dtc) (2) in acetone solution. Colourless needles were obtained, m.p. 134-136°C.

Anal. Found: C, 56.4; H, 4.4; Au, 22.7. Calc. for (Ph₃P)ₓAu(Et₂dtc): C, 56.6; H, 4.6; Au, 22.6%.

(Ph₃P)Au(Et₂dtc) was prepared by adding equivalent amounts of Na(Et₂dtc).3H₂O (Fluka A.G.) in ethanol to a solution of (Ph₃P)AuCl (3) in CH₂Cl₂. 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°C.

Anal. Found: C, 46.0; H, 4.1; N, 2.3; S, 10.5; Au, 32.4%. Calc. for (Ph₃P)Au(Et₂dtc): C, 45.5; H, 4.1; N, 2.3; S, 10.6; Au, 32.5%.

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