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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 $[\ (Ph_3P)_2M(R_2dtc)\ ]$ 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 $(Ph_3P)_2M^+.R_2dtc^-$. We have reinvestigated the Et_2dtc complexes, and have also succeeded in preparing $(Ph_3P)_2Au(Et_2dtc)$. 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 $ohm^{-1}cm^2mole^{-1}$). Osmometrically determined molecular weights are summarized in the TABLE. The combined results clearly indicate a dissociation:

$$(Ph_3P)_2M(R_2dtc) \rightleftharpoons (Ph_3P)M(R_2dtc) + Ph_3P$$

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 $(Ph_3P)Au(Et_2dtc)$ which is monomeric in benzene solution (TABLE).

Attempts to prepare $(Ph_3P)M(Et_2dtc)$ ... 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

TABLE

Molecular weights of $(Ph_3P)_2M(Et_2dtc)$ and $(Ph_3P)Au(Et_2dtc)$ in benzene at 37°.

	Found	Calc.
$(Ph_3P)_2Cu(Et_2dtc)$	600	736
$(Ph_3P)_2Ag(Et_2dtc)$	450	781
$(Ph_3P)_2Au(Et_2dtc)$	430	870
$(Ph_3P)Au(Et_2dtc)$	600	607

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.
$(Ph_3P)_2M(Et_2dtc)$ ... M = Cu, Ag were prepared as previously reported (1).
$(Ph_3P)_2Au(Et_2dtc)$ was prepared on addition of two moles Ph_3P to 1 mole $Au(Et_2dtc)$ (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 $(Ph_3P)_2Au(Et_2dtc)$: C, 56.6; H, 4.6; Au, 22.6%.
$(Ph_3P)Au(Et_2dtc)$ was prepared by adding equivalent amounts of $Na(Et_2dtc).3H_2O$ (Fluka A.G.) in ethanol to a solution of $(Ph_3P)AuCl$ (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 $(Ph_3P)Au(Et_2dtc)$: C, 45.5; H, 4.1; N, 2.3; S, 10.6; Au, 32.5%.

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