INORG. NUCL. CHEM. LETTERS Vol. 7, pp. 87-89, 1971. Pergamon Press. Printed in Great Britain.

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).

(Received 7 August 1970)

The synthesis and properties of bis-triphenylphosphine complexes of Cu(I) and Ag(I) N, N-dialkyldithiocarbamates [(Ph3P)2M(R2dtc)] 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 (Ph3P)2M⁺.R2dtc⁻. We have reinvestigated the Et₂dtc complexes, and have also succeeded in preparing (Ph3P)2Au(Et2dtc). Conductivity studies in nitrobenzene show the Cu, Ag and Au complexes to be non-electrolytes (at a concentration of 10^{-2} mole/1 the molar conductivity is lower than 0.1 ohm⁻¹cm²mole⁻¹). Osmometrically determined molecular weights are summarized in the TABLE. The combined results clearly indicate a dissociation:

 $(Ph_3P)_2M(R_2dtc)$ + Ph_3P

It is noteworthy that the dissociation increases in the order $Cu \lt Ag \lt Au$. 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 $(Ph_3P)M(Et_2dtc) \dots M = Cu$, 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 $(Ph_3P)_2M(Et_2dtc)$ and $(Ph_3P)Au(Et_2dtc)$ in benzene at 37° .

	Found	Calc.
(Ph ₃ P) ₂ Cu(Et ₂ dte)	600	736
(Ph ₃ P) ₂ Ag(Et ₂ dtc)	450	781
(Ph ₃ P) ₂ Au(Et ₂ dtc)	430	870
(Ph ₃ P)Au(Et ₂ dtc)	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. $(Ph_3P)_{2}M(Et_{2}dtc)$... M = Cu, Ag were prepared as previously reported (1). (Ph3P)2Au(Et2dtc) was prepared on addition of two moles Ph_3P to 1 mole Au(Et₂dtc) (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 (Ph₂P)₂Au(Et₂dtc): C, 56.6; H, 4.6; Au, 22.6%. (Ph₂P)Au(Et₂dtc) was prepared by adding equivalent amounts of $Na(Et_{dtc})$. 3H₂O (Fluka A.G.) in ethanol to a solution of $(Ph_3P)AuCl(\bar{3})$ 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 (Ph₃P)Au(Et₂dtc): C, 45.5; H, 4.1; N, 2.3; S; 10.6; Au, 32.5%.

ACKNOWLEDGEMENT

The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research.

REFERENCES

- 1. C. Kowala and J.M. Swan, Austr.J.Chem., 19, 555 (1966).
- 2. S. Akerström, Arkiv Kemi, <u>14</u>, 387 (1959).
- 3. F.G. Mann, A.F. Wells and D. Purdie, J.Chem.Soc., 1828 (1937).