

Triphenylphosphine–Gold(0)gold(I) Compounds

By L. MALATESTA, L. NALDINI, G. SIMONETTA, and F. CARIATI

(Istituto di Chimica Generale e Inorganica, Università di Milano, Italy)

PREVIOUSLY we found that the halogenotriphenylphosphine derivatives of copper and silver gave the compound L_2MBH_4 [$L = P(C_6H_5)_3$, $M = Cu, Ag$]^{1,2} by reaction with sodium borohydride. By reaction of chlorotriphenylphosphinegold(I) with sodium borohydride in ethanol we obtained a red compound almost insoluble in ethanol, slightly soluble in chloroform and dichloromethane, and which did not contain boron. The fact that it did not contain hydride hydrogen was confirmed by the i.r. spectrum, both in the solid state and in solution. The compound corresponded analytically to $Au_5L_4Cl \cdot 3 \cdot 5H_2O$ (I). (Found: C, 40·4; H, 3·1; Au, 46·2; Cl, 1·7; P, 5·8. $C_{72}H_{60}Au_5ClP_4 \cdot 3H_2O$ requires: C, 40·75; H, 3·1; Au, 46·4; Cl, 1·7; P, 5·8%. $C_{72}H_{60}Au_5ClP_4 \cdot 4H_2O$ requires: C, 40·35; H, 3·2; Au, 46·1; Cl, 1·7; P, 5·8%. This same compound was also obtained by using as reducing agent lithium aluminium hydride or ethanolic

potassium hydroxide. Compound (I) by digestion in cold methanol slowly dissolved giving $Au_5L_4Cl \cdot 4CH_3OH$ (II). (Found: C, 41·5; H, 3·4; Au, 44·7; Cl, 1·6; P, 5·6. $C_{72}H_{60}Au_5ClP_4 \cdot 4CH_3OH$ requires: C, 41·45; H, 3·5; Au, 44·85; Cl, 1·6; P, 5·65%.) Compounds (I) and (II) had an ionic structure: in fact, by exchange reaction with nitrate, perchlorate, and tetraphenylborate anions, compound (II) gave the corresponding salts which all behaved as uni-univalent electrolytes like compound (II) itself.

The behaviour of compound (II), when it was heated under reflux in ethanol, was found to be in accordance with the formula reported above in which we may consider one atom of gold as having oxidation-number (I), and the other four as having oxidation-number zero: in fact, when its methanolic solution was heated under reflux in an inert atmosphere for 24 hr., 4/5 of the gold was separated

¹ F. Cariati and L. Naldini, *Gazzetta*, 1965, **95**, 201.

² F. Cariati and L. Naldini, *Gazzetta*, in press.

as metal while 1/5 was recovered from the solution as AuClL_2 .

All these compounds were found to be diamagnetic: this diamagnetism indicated the presence of an interaction between the gold(0) atoms, so as to couple the electrons in the half-filled 6s orbitals. The stability of metal-to-metal bonds for Group Ib metals, and particularly for gold, has been emphasized by Nyholm, who prepared a series of compounds of the type $(\text{LAu})_n\text{-ML}'_m$,³ none of which however had gold-to-gold bonds. In our case, in addition to these bonds, which should be considerably delocalized among the four gold(0) atoms, there must be other interactions between the gold(I)

atoms, which we suppose to be in a central position, and the gold(0) atoms: probably some kind of three-centre bond could be formed by overlapping of the sp hybrid orbitals of gold(I) with the s orbitals of gold(0) atoms.

Compound (I) reacted with potassium cyanide giving $\text{Au}_3(\text{CN})\text{L}_2$, a very insoluble red crystalline substance, in which the cyanide group appeared to be covalently bonded, as proved by the position of the CN stretching band in the i.r. spectrum. We are now trying to obtain single crystals of these compounds in order to determine their structure.

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C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.* 1964, 1741.