

Gold-Tertiary Phosphine Derivatives with Intermetallic Bonds

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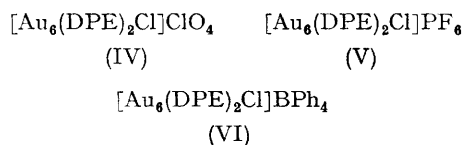
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WE have reported previously¹ on the reaction of sodium borohydride with the triphenylphosphine-halogeno-derivatives of the metals of Sub-group IB.

We have now commenced studies on the reaction of sodium borohydride on phosphine-gold halides having as ligand 1,2-bisdiphenylphosphine-ethane (DPE) instead of triphenylphosphine, with the purpose of studying the influence of the ligand on the type of compound. This chelating phosphine is more basic than triphenylphosphine, and has different steric requirements.

The product of the reaction of ClAu(DPE)AuCl with sodium borohydride was a brown compound which corresponded analytically to Au₆(DPE)₂Cl₂·2EtOH (I), and which by exchange with lithium bromide and iodide gave the corresponding halogeno-derivatives: Au₆(DPE)₂Br₂·2H₂O (II) and Au₆(DPE)₂I₂·2H₂O (III). On the other hand, by exchange with the lithium or sodium salts of anions with low nucleophilic character such as perchlorate, hexafluorophosphate, and tetraphenylborate only one chloride ion was exchanged, indicating that the two chlorine atoms are not equivalent. The diamagnetic compounds which were obtained in this

way behave as uni-univalent electrolytes in nitromethane solution and we consider therefore that the halogen atom which is not replaced is covalently bound to the cations:



The far-infrared spectra of compounds (I), (IV), (V), and (VI) showed a band of medium intensity at 288 cm.⁻¹ By comparison with the chlorine-to-metal band of ClAu(DPE)AuCl at 325 cm.⁻¹, we assign this band, shifted to lower wavenumber, to a bridging chloride.

The complex cation might be then speculatively considered as formed by two clusters of three gold atoms, having one chlorine and two DPE bridges. We suggest that each of the two clusters contains three neutral gold atoms less one 6s-electron, held together by a three-centre molecular orbital containing two electrons. This type of cluster

would be similar to that present in Au_3L_2CN ;^{1e} the more basic phosphorus atom of DPE would transfer to the metal more electronic charge than triphenylphosphine, and this would compensate for the smaller charge donated by the bridging chloride ion.

The bromo- and iodo-compounds (II) and (III) respectively, should be considered as analogous to the chloro-derivative (I), but the presence of the bridging halogen has not been confirmed by i.r. spectra because the metal-halogen stretching was beyond the limit of our apparatus.

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¹ (a) F. Cariati and L. Naldini, *Gazzetta*, 1965, **95**, 3; (b) F. Cariati and L. Naldini, *ibid.*, p. 201; (c) F. Cariati and L. Naldini, *J. Inorg. Nuclear Chem.*, 1966, **28**, in the press; (d) L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Chem. Comm.*, 1965, 212; (e) L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, "Coordination Chemistry Reviews," Elsevier, Amsterdam, 1966.