Crystal Structure and Ligand Mobility in Solution of cis-Dimethyl-bis(trimethylphosphine)gold(III) Complexes

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Complexes $[Me_2Au(PMe_3)_2]^+$ X^- with X = I and ClO_4 have been prepared by several conventional routes in good yields. The products are thermally stable and decompose above 130 °C with reductive elimination of ethane. The two salts crystallize as isomorphous orthorhombic dichloromethane solvates. The cations have the *cis*-configuration based on a crystallographically imposed C_{2v} symmetry. Owing to the *trans* influence of the tertiary phosphine ligands the Au-C bonds are significantly shorter than in standard reference cases. The cations are stacked in pairs of columns running parallel to the *c* axis of the unit cell with the Me₂Au units oriented in opposite directions and slightly interlocked. The anions are inserted into the pockets formed by the four Me₃P groups of each pair of neighbouring cations in the same column. The large channels between the double columns are filled by the solvent molecules, which could be localized for the perchlorate salt, but were disordered and deficient in the iodide case.

Key words: Gold(III) Complexes, Dimethylgold(III) Complexes, Ligand Exchange, trans Influence, Crystalline Solvates