

Variations in the Chain Structure of Cationic (Phosphine)gold(I) Dialkyldithiophosphate Complexes

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Treatment of dithiophosphoric acid diesters $(\text{RO})_2\text{P}(\text{S})\text{SH}$ with appropriate quantities of tris[(phosphine)gold(I)]oxonium tetrafluoroborates $\{[(\text{R}'_3\text{P})\text{Au}]_3\text{O}\}^+ \text{BF}_4^-$ in dichloromethane gives di- or trinuclear complexes of the types $\{(\text{RO})_2\text{P}[\text{SAu}(\text{PR}'_3)]_{2/3}\}^{+/2+}$ (2) BF_4^- as colourless, crystalline salts. As determined by single crystal X-ray diffraction studies, in the 1:2 complexes (with $\text{R} = \text{R}' = \text{Me}$ and $\text{R}' = \text{Et}$, $\text{R} = \text{Ph}$ and *o*-Tol), each gold atom is attached to a different sulfur atom, but with short intracationic Au–Au contacts. These cations are associated to form strings through intermolecular Au–Au contacts in the first case ($\text{R} = \text{Et}$), but through additional Au–S contacts in the second ($\text{R} = \text{Ph}$). For $\text{R} = \text{o-Tol}$, the cations are not associated at all owing to steric hindrance. This result is indicative of very small energy differences between the two modes of association. The 1:3 complexes are fluxional in solution and show virtually equivalent R_3PAu groups in the NMR spectra at 20°C, but at low temperature non-equivalent ligands can be distinguished as shown previously for analogous dithiophosphinate derivatives.

Reprint requests to Prof. Dr. H. Schmidbaur.