

Preparation, Structure and Gold(I) Complexation of *p*-Xylylene-1,4-diphosphines

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Dedicated to Professor Alfred Schmidpeter on the occasion of his 75th birthday

1,4-Dimethyl-2,5-di(phosphinyl)benzene (**1**) was prepared in high yield in a four-step synthesis from 1,4-dibromo-2,5-dimethyl-benzene. The intermediates with (Et₂N)₂P and Cl₂P groups (**2**, **3**) with the corresponding substitution pattern have been isolated and structurally characterized. All three compounds (**1**–**3**) adopt a centrosymmetrical conformation with one of the P-X bonds of each X₂P group located in the ring plane while the other reaches out from this plane in a roughly perpendicular orientation. Distortions of the ring and its substituents from a standard planar hexagonal geometry are readily explained by invoking steric and inductive effects. The crystal structure of 1,4-dibromo-2,5-dimethyl-benzene has also been determined for reference purposes. Compound **1** was employed as a substrate for auration by tri(gold)oxonium salts of the type {[(R₃P)Au]₃O } BF₄. Hexanuclear complex salts of the type {[(R₃P)Au]₃P(C₆H₂Me₂)P[Au(PR₃)]₃ } (BF₄)₂ were obtained in almost quantitative yield with R₃P = ^tBu₃P (**4**) and Ph₃P (**5**). The former (**4**) has the higher thermal stability, it could be crystallized and its structure determined. It features a conformation in which the xylene plane bisects one of the Au-P-Au angles at both tetrahedrally coordinated central phosphorus atoms placing its methyl groups in sterically least hindered positions. Compound **5** is labile in solution and shows rapid ligand exchange on the NMR time scale. The limited stability has also been confirmed by mass spectrometry. Similar structural details and differences in stability were observed in the related trinuclear gold complexes based on 1-naphthyl-phosphine, which were prepared as reference materials using the same preparative procedure. Of the two compounds {[(1-C₁₀H₇)-P[Au(PR₃)]₃ } BF₄, with R₃P = ^tBu₃P (**6**) and Ph₃P (**7**), the former is the more stable species. In the solid state the cation approaches mirror symmetry in a conformation comparable to that of **4**. Compound **7** is thermally labile and shows a rapid ligand exchange in solution.

Key words: Primary Phosphines, Phenylene-1,4-diphosphines, Gold Complexes