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Spectroscopic study of phosphine selenide complexes of Au(I) and X-ray structure of [(cyclohexyl)$_3$PSeAuBr]

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The X-ray structure determination of the complex, [(cyclohexyl)$_3$PSe-AuBr], revealed a triclinic space group P-1, with $a = 9.7654(7)$, $b = 10.9441(9)$, $c = 11.2064(9)$ Å, $\alpha = 117.076(6)^\circ$, $\beta = 99.076(6)^\circ$, $\gamma = 95.417(6)^\circ$, $V = 1034.07(14)$ Å^3 and $Z = 2$. The Au(I) atom in this complex has a linear coordination with Se1 atom at 2.3776(9) Å on one side and Br1 at 2.3843(9) Å at the trans position making the Se1-Au1-Br1 angle of 177.97(4)°. The P1 atom in the phosphine has tetrahedral geometry. All three cyclohexyl groups are in their usual boat conformation. The phosphorus atom of the triphenylphosphine is approximately perpendicular to the Se1−Au1−Br1 linkage with P1−Se1−Au1 angle of 99.19(6)°. The $\Delta\delta$ in the ^{31}P NMR of the free ligands and their corresponding L−Se−Au−Br (L−Se = trialkyl/arylphosphine selenides) complexes, and the changes in the P−Se bond frequencies in the FTIR upon complexation, are indicative of the bonding of the ligand to Au(I) through selenium. There is a strong corelation between the chemical shifts of the ^{31}P NMR and the C−P−C angle in the phosphines.

KEY WORDS: Phosphine selenide; Au(I); X-ray structure.

Introduction

We have recently reported the synthesis, X-ray structure, and the solution equilibrium of cyanogold complexes of a series of phosphines [R_3P] with R = phenyl, cyclohexyl, and 2-cyanoethyl.[1–3] All phosphine complexes reported so far, form linear monomeric species with cyanogold(1) except tri(2-cyanoethyl)phosphine (CEP) which yielded an ionic dimeric complex [$(CEP)_3Au$][$Au(CN)_2$] with AuCN and even when AuCN was replaced by AuBr or AuCl.[4,5] A large formation constant of $[Au(CN)_2]^-$ in addition to the unique electronic characteristics of CEP are believed to cause ligand dispropotionation of the monomeric [(CEP)AuCN] initially formed which finally gets converted into an ionic species.[6]

The synthetic and crystallographic studies of gold complexes of phosphines were undertaken because of their similarity to several anti-arthritic gold drugs.[7] Recent research has suggested that heavy-metal toxicity is reduced if selenium derivatives are employed.[8] An understanding of the structure of the title complexes might aid in understanding the chemistry of the gold–selenium bond which provides further insight into the biochemical mechanism of gold–selenium drugs.[9] The present study was prompted to investigate the effects of steric and electronic characteristics of phosphines with respect to the formation of monomers *versus* ionic complexes.

Experimental section

Preparation of the complexes

The crystalline complexes were prepared by mixing equimolar amounts of acetone solution of the corresponding phosphine selenide and an aqueous solution of $AuBr{\cdot}2H_2O$ using the procedure reported in the literature.[10] All complexes precipitated

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