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Synthesis, characterization, structure and luminescence studies of dinuclear gold(I) alkynyls of bis(diphenylphosphino)alkyl- and aryl-amines

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Dedicated to Professor D.M.P. Mingos.

Abstract

A series of alkynylgold(I) bis(diphenylphosphino)alkyl- and aryl-amine complexes, $[\{Ph_2PN(R)PPh_2\}Au_2(C{\equiv}CR')_2]$ [R = ^{n}Pr, R′ = Ph (**1**), C_6H_4OMe-*p* (**2**), C_6H_4Me-*p* (**3**), C_6H_4Cl-*p* (**4**); R = C_6H_4OMe-*p*, R′ = Ph (**5**)], has been synthesized. The X-ray crystal structures of **1** and **2** revealed the presence of short intramolecular Au···Au contacts with the distances of 2.8404(8) and 3.0708(7) Å. The luminescence behavior of the complexes were studied.

Keywords: Gold(I); Alkynyl ligands; Luminescence; Phosphine ligands

1. Introduction

During the last decade, the synthesis, molecular structures and chemistry of gold(I) phosphine alkynyl complexes have attracted much attention, in part due to the reports on their rich luminescence properties and their ability to build supramolecular structures based on the aurophilic nature of gold [1]. There has also been a growing interest in the study of dinuclear gold(I) alkynyl complexes with bidentate phosphine ligands, as it was believed that the presence of bidentate phosphines would bring the two gold atoms into close proximity to have weak metal–metal interactions that conferred them the rich luminescence properties. However, most of the gold(I) complexes involved the use of phosphines with P–$(CH_2)_n$–P unit [2,3], and examples with $Ph_2PN(R)$-PPh_2 ligands were limited [4]. Recently, bis(diphosphino)-amine-type ligands have proved to be very versatile because substituents on both phosphorus and nitrogen atoms could be varied with attendant changes in the P–N–P bond angle and the conformation around the phosphorus centers [4,5]. As an extension of our recent interest in d^{10} metal complexes with bis(diphosphino)amine-type ligands [4d–g], herein are reported the synthesis, characterization, structure and luminescence studies of a series of alkynylgold(I) bis(diphenylphosphino)alkyl- and aryl-amine complexes, $[\{Ph_2PN(R)PPh_2\}Au_2(C{\equiv}CR')_2]$ [R = ^{n}Pr, R′ = Ph (**1**), C_6H_4OMe-*p* (**2**), C_6H_4Me-*p* (**3**), C_6H_4Cl-*p* (**4**); R = C_6H_4-OMe-*p*, R′ = Ph (**5**)]. The X-ray crystal structures of **1** and **2** have been determined.

2. Results and discussion

2.1. Syntheses and characterization

The alkynylgold(I) bis(diphenylphosphino)alkyl- and aryl-amine complexes were prepared by modification of

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the literature procedures [1e,3b]. Instead of reaction of alkynes with $(PR_3)AuCl$ in the presence of a base such as NaOEt or NaOMe [1b,3d,6], the complexes were synthesized by the depolymerization reaction of $[Au(C{\equiv}CR)]_\infty$ with phosphine ligands. All the newly synthesized complexes have been characterized by ^1H NMR, ^{31}P NMR, and IR spectroscopy and positive-ion FAB-mass spectrometry, and gave satisfactory elemental analyses. The structures of complex **1** and **2** were determined by X-ray crystallography.

The IR spectra of all the alkynylgold(I) complexes showed weak intensity absorption bands at ca. 2081–2122 cm^{-1}, typical of the $\nu(C{\equiv}C)$ stretch of the alkynyl unit. The ^1H NMR spectra of all the complexes showed resonance signals and coupling patterns that were consistent with their chemical formulations. Complexes **1**–**5** showed a singlet in the $^{31}P\{^1H\}$ NMR spectra, indicating that all the phosphine groups on the complexes were chemically and magnetically equivalent.

2.2. Crystal structure determination

The perspective drawings of complexes **1** and **2** were depicted in Figs. 1 and 2, respectively. The crystal structure determination data of **1** and **2** were listed in Table 1. Selected bond distances and angles for **1** and **2** were summarized in Tables 2 and 3, respectively.

The X-ray crystal structures of **1** and **2** showed C–Au–P angles of 173.3(2)–176.2(3)°, which deviated slightly from the idealized geometry of 180°, probably as a result of the steric demand of the ligand or crystal packing forces. The C≡C bond lengths in the range of 1.180(11)–1.246(16) Å in **1** and **2** were typical of terminal alkynylgold(I) systems [1b,3b-d,6b,7]. The C≡C bond distances of complex **1** were slightly longer than that of **2**, probably resulted from the C–H···$\overset{C}{\underset{C}{\|}}$ contact found in the crystal packing, in which the aromatic proton of one molecule interacted with one of ethynyl groups on the adjacent molecule. The Au–C distances of complexes **1** and **2** were in the range of 2.013(10)–2.134(14) Å.

The intramolecular Au···Au distances of complexes **1** and **2** were 2.8404(8) and 3.0708(7) Å, respectively, indicative of the presence of Au···Au interactions. The intramolecular Au···Au distances of complex **1** was short compared to that of other dinuclear gold(I) phosphine complexes, such as $[(dppm)_2Au_2]Cl_2$ (2.962(1) Å) [8], and $[(dmpm)_2Au_2](ClO_4)_2$ (3.028(2) Å) [9]. The arrangements of the two adjacent Au(C≡CPh) groups in **1** and Au(C≡CC_6H_4OMe-*p*) groups in **2** were found to be in a crossed geometry, in which the C–Au–Au–C torsion angles of complexes **1** and **2** were 32.5(8)° and 37.1(4)°, respectively.

It was interesting to note that in the alkynylgold(I) complexes with P–$(CH_2)_n$–P moiety, reaction of $[Au(C{\equiv}CPh)]_\infty$ with dppm gave the trinuclear complex, $[Au_3(dppm)_2(C{\equiv}CPh)_2][Au(C{\equiv}CPh)_2]$, rather than a dinuclear complex, in which the trinuclear cation with three gold atoms adopted an isosceles triangular arrangement with intramolecular Au···Au distances of 3.083(2) and 3.167(2) Å [3b], while using the slightly longer P–$(CH_2)_2$–P moiety, the dinuclear alkynylgold(I) complex, $[Au_2(dppe)(C{\equiv}CPh)_2]$, was obtained which was found to show an intermolecular Au···Au distance of 3.153(2) Å [3a] in its X-ray crystal structure.

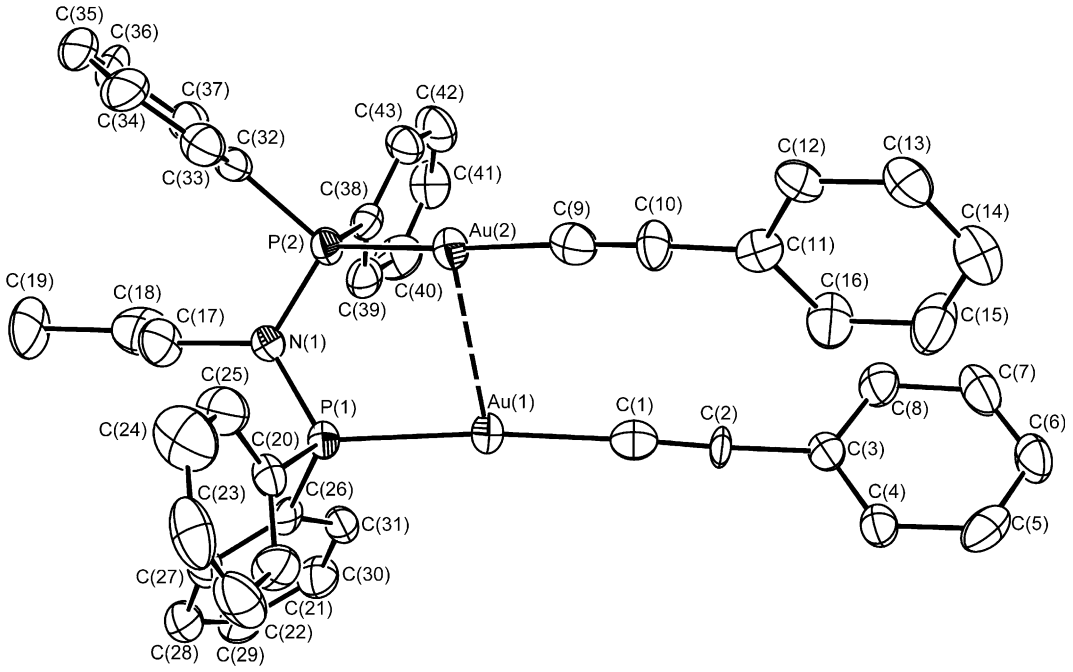

Fig. 1. Perspective view of $[\{Ph_2PN(^nPr)PPh_2\}Au_2(C{\equiv}CPh)_2]$ (**1**) with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 30% probability level.