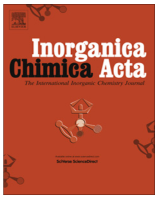
Inorganica Chimica Acta 406 (2013) 293–300

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Synthesis, X-ray crystallography, and photoluminescence studies of four coordinate gold(I) complexes with the weak Lewis base tri-2-furyl phosphine ligand

Darkus E. Jenkins [a], Richard E. Sykora [b], Zerihun Assefa [a,*]

[a] Department of Chemistry, North Carolina A&T State University, Greensboro, NC 27411, USA
[b] Department of Chemistry, University of South Alabama, Mobile, AL 36688, USA

ARTICLE INFO

Article history:
Received 4 November 2012
Received in revised form 16 April 2013
Accepted 23 April 2013
Available online 13 May 2013

This paper is dedicated to Professor Solomon Bililign on the occasion of his 60th birthday celebration. Professor Bililign has been an esteemed scientist, a mentor and colleague over the years and we wish him several more years of active contribution to the chemical physics community.

Keywords:
Gold(I)
Tri-2-furyl phosphine
Photoluminescence
Four coordinate
Tetrahedral
X-ray crystallography

ABSTRACT

The synthesis and structural characterization, and luminescence properties of two new four-coordinate gold(I) complexes containing the monodentate tri-2-furly phosphine is described. The gold(I) center easily accommodates up to four of the phosphine ligands forming a nearly tetrahedral geometry. Formation of four-coordinate gold(I) species is favored mainly due to electronic factors since the cone angle of the ligand is larger than several other alkyl phosphines hitherto unknown to form four coordination. In the complexes the gold center has a nearly regular tetrahedral geometry with an average P–Au–P angle of 109.37°. The crystal structure of $[Au(TFP)_4]Cl\cdot CH_3CN$, **3**, reveals four phosphine ligands bound to the gold(I) atom as well as free Cl^- and CH_3CN within the crystal lattice providing a nearly regular tetrahedral geometry with an average P–Au–P angle of 109.4°. The photo-luminescent properties of the complexes are compared with that of the ligand and show ligand centered emission perturbed by the metal coordination. DFT theoretical calculations were also conducted and support the assignment of the spectroscopic data.

1. Introduction

A number of tertiary phosphines are known to coordinate to a gold(I) center [1–9]. Only a small number of ligands have been found capable of providing four-coordinate tetrahedral geometry with the gold(I), most of them being either bidentate phosphines [2,10] and/or thiolate ligands [11,12]. However, structurally characterized three or four-coordinate gold(I) complexes with monodentate phosphines are limited; the 1,3,5-triaza-7-phosphaadamantane (TPA) [13] and methyl-diphenyl phosphine ($MePPh_2$) [14] ligands are noteworthy to mention. Strong arguments that the ability of TPA to form stable four coordinate gold(I) complexes is based on the small cone angle of 102° [13]. Although a small cone angle clearly supports higher coordination at the gold center, consideration of electronic factors is also important in dictating higher coordination numbers. Interest in three- or four-coordinate phosphine or thiolate complexes of gold are gaining reputation as effective therapeutic agents in the treatment of rheumatoid arthritis and in cancer therapy [2]. Moreover, gold-phosphane complexes are highly important for homogeneous catalysis, where the four coordinated diphosphane diorgano complexes are assumed to be the intermediates in the process [15]. A particularly interesting application of high coordination gold(I) complexes is related to the fact that three-coordinate species generally have luminescent properties that can be exploited for light-emitting diodes [16].

Although the chemical reactivities of R_3P phosphines are by in large determined by two factors, steric and electronic, these properties are closely inter-related [17]. The increase in the steric bulk of the R groups is known to reduce the σ-character of the phosphorous lone pair, and therefore makes these ligands stronger Lewis bases [17].

Tertiary phosphines with heterocyclic substituents have attracted a great deal of attention in the design and development of tailor-made ligands for transition metal coordination [18] and important organic reactions. Gold coordination of phosphine

---

* Corresponding author. Address: Department of Chemistry, North Carolina A&T State University, 1601 E. Market St., Greensboro, NC 27455, USA. Tel.: +1 336 285 2255; fax: +1 336 334 7124.
E-mail address: zassefa@ncat.edu (Z. Assefa).

0020-1693/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2013.04.047

ligands with heterocycles bearing potentially coordinating heteroatoms on the carbon next to phosphorous have been studied in limited cases. A recent example involves a phoshphane system containing 2-pyridyl groups, viz (diphenyl(2-pyridyl)phosphane) that provided interesting structural features including characterization of the first structure of a polymeric tricoordinate gold(I) complex containing a chiral phosphane ligand [19].

Similarly, we have been interested in the coordination of tri-2-furylphosphine ligands to gold(I) centers, that contain an oxygen atom bonded to a carbon next to the phosphorous atom. The steric properties of the tri-2-furyl phosphine (TFP) ligand are comparable to triphenylphosphine (PPh_3), in terms of cone angle, where the TFP at 133° is only slightly smaller than that of PPh_3 (145°) [18]. Although these two ligands can be considered similar sterically, their electronic properties are different because of the presence of the strong electron withdrawing tri-2-furyl groups in the former [18]. The TFP ligand is thought to be a poor π-electron donor whereas PPh_3 is a strong π-electron donor [18]. Due to its unique electronic behavior, TFP has been used in a variety of chemical reactions including metal-catalyzed cross-coupling reactions [18,20–23].

Hence it was of interest to explore the effect of electronic factors in dictating the coordination number of the poor Lewis donor TFP ligand to a gold(I) center, where its low donor effect is expected to stabilize the high electron count on the metal center [20,24]. The phosphorus bound to three furyl rings offers sustainability for the strong electron withdrawing effect found with TFP, while the oxygen atoms of the furyl rings have shown no support in coordination to metal atoms [24].

Although, the electronic consequences of the TFP ligand are unique, its coordination chemistry with gold(I) has not been detailed extensively beyond the mono-coordinated gold(I) chloride system [24–26]. Tiekink and co-workers were the first group to report the X-ray crystal structure of the Au(TFP)Cl [26]. However, it was the Schmidbaur group that explored the preferential coordination of phosphorus to gold(I) in the Au(TFP)Cl system and compared it with tri(2-thienyl)phosphine [25].

Here, we report the coordination of the TFP ligand to a gold(I) center. The structural analysis, luminescence studies and results from theoretical DFT calculations are compared for the complexes that are coordinated with one, three and four TFP ligands. In view of the fact that most of the alkyl phosphines with significantly smaller cone angles are not known to form four-coordination, it might be of interest to understand the electronic consequences of the furyl group in stabilizing higher coordination in gold.

2. Experimental

2.1. General method

All reactions were carried out under a modified Schlenk technique at room temperature. Tetrahydrothiophene gold(I) chloride (thtAuCl) is prepared according to literature [27]. The IR spectra were collected with potassium bromide (KBr) pellets on a Mattson Instruments 2020 Galaxy Series Fourier-transform infrared spectrophotometer, over the 4000–350 cm^{-1} range. ^1H and ^{31}P NMR spectra were recorded on a 300 MHz Varian NMR 300-411149 FT-NMR spectrometer. Chemical shifts [δ (ppm)] were reported relative to Me_4Si and 85% H_3PO_4 in $CDCl_3$ (if no other solvent is stated).

2.2. Synthesis

2.2.1. Synthesis of chloro-tri-2-furyl phosphine gold(I), [Au(TFP)Cl] (**1**)

To 0.1 g (0.312 mmol) of thtAuCl was added 10 mL of THF in a 25 mL round bottom flask. A 0.071 g (0.306 mmol) of TFP was then added and the solution stirred for 3 h. The solvent was partially removed by blowing the flask with nitrogen gas. The remaining mixture was then placed in a refrigerator overnight, where colorless product was obtained. Recrystallization was conducted by dissolving the product in a 2:1THF:Et_2O mixture. Partial evaporation of the solvent and overnight refrigeration provided X-ray quality crystals. Yield of **1** is 95%. ^1H NMR in chloroform [δ (ppm)]: 6.73(m), 7.51(s), and 7.98(m). ^{31}P NMR [δ (ppm)]: −29.03. *Anal.* Calc. for $AuPClO_3H_9C_{12}$: C, 31.02; H, 1.96. Found: C, 31.34; H, 1.38%.

2.2.2. Synthesis of chloro tris(tri-2-furyl phosphine) gold(I), $[Au(TFP)_3Cl]$ (**2**)

A 0.1 g (0.312 mmol) of thtAuCl was added into a 25 mL round bottom flask discharged with 10 mL THF, and a 0.21 g (0.936 mmol) TFP ligand was then added into the flask; the solution was then stirred for 3 h. The mixture was then purged using nitrogen gas until a small amount of the solvent remained. The remaining product was placed in a refrigerator overnight, and was recrystallized by dissolving in a 2:1THF:Et_2O mixture. Partial evaporation and overnight refrigeration provided colorless crystals. Yield of **2** is 80%. ^1H NMR in chloroform [δ (ppm)]: 6.54(m), 7.02(s), 7.79(m). ^{31}P NMR [δ (ppm)]: −11.61. *Anal.* Calc. for $AuP_3ClO_9H_{27}C_{36}$: C, 46.55; H, 2.93. Found: C, 50.25; H, 3.57%.

2.2.3. Synthesis of tetrakis(tri-2-furyl phosphine) gold(I) chloride acetonitrile solvate, $[Au(TFP)_4]Cl\cdot CH_3CN$ (**3**)

A 0.1 g (0.312 mmol) of thtAuCl was added to a 50 mL round bottom flask containing 10 mL of 1:1 THF/CH_3CN mixture. A 0.072 g (0.310 mmol) of TFP was then added to the solution. After stirring for 1 h a 0.053 g (0.312 mmol) of $AgNO_3$ was added and the solution stirred for additional 10 min. The mixture was filtered to collect the white solid formed. To the filtrate 0.217 g (0.936 mmol) of TFP was added and stirred for 1 h and then filtered. The mixture was then purged using nitrogen gas until most of the solvent was removed. The remaining product was placed in a refrigerator overnight. The product was recrystallized by dissolving in a solvent mixture of 2:2:1 mL of THF:CH_3CN:Et_2O, respectively. Partial evaporation and overnight refrigeration provided colorless crystals. Yield of **3** is 80%. ^1H NMR ($CHCN_3$)[δ (ppm)]: 6.61(m), 7.31(s), 7.84(m). ^{31}P NMR in acetonitrile [δ (ppm)]: −13.94. *Anal.* Calc. for $AuP_4ClO_{12}H_{36}C_{48}$: C, 49.91. Found: C, 50.19%.

2.3. X-ray structure determination of **1–3**

All of the X-ray data collections were performed on an Enraf–Nonius CAD-4-PC diffractometer using CAD-4-PC software for control and cell refinement. *XCAD4*[28] was used to process the raw X-ray data. The structures were solved using the SHELXS97 program by direct methods. The SHELXL97 program [29] was used to refine the structures, while molecular graphics were created using the OLEX2 [30]. The molecular structures for **2** and **3** are presented in Figs. 1 and 2, respectively. The crystallographic and structural refinement data for **2** and **3** are summarized in Table 1.

2.4. Photoluminescence studies

The steady-state excitation and emission spectra were obtained on a Photon Technology International (PTI) spectrometer model QM-3 instrument with a steady state Xe excitation source, and photomultiplier detection system. Selection of excitation and emission wavelengths are conducted by means of computer controlled, autocalibrated “QuadraScopic” monochromators which are equipped with aberration corrected emission and excitation optics. Signal detection is accomplished with PMT detectors (model 928 tube) that can work either in analog or digital (photon counting) modes. The instrument operation, data collection, and