

## Three- and Four-Coordinate Gold(I) Complexes of 3,6-Bis(diphenylphosphino)pyridazine: Monomers, Polymers, and a Metallocryptand Cage

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The slightly yellow polymeric complexes  $\{\text{Au}_2\text{Cl}_2(\text{P}_2\text{pz})_3\}_n$ , **1**·6CHCl<sub>3</sub>, (P<sub>2</sub>pz is 3,6-bis(diphenylphosphino)pyridazine) and  $\{[\text{Au}_2(\text{P}_2\text{pz})_3](\text{PF}_6)_2\}_n$ , **2**, are prepared by the stoichiometric reaction of AuCl(tht) (tht is tetrahydrothiophene) and P<sub>2</sub>pz in either dichloromethane or dichloromethane/methanol, respectively. Addition of 2 equiv of AuCl(tht) to a dichloromethane solution of 1 equiv of P<sub>2</sub>pz generates the simple (AuCl)<sub>2</sub>(P<sub>2</sub>pz) compound, **3**. Compound **3** contains nearly linear P–Au–Cl units with intermolecular Au···Au separations of 3.570 Å. Au<sub>2</sub>l<sub>2</sub>(P<sub>2</sub>pz)<sub>3</sub>, **4**, is prepared by reacting excess NaI with **2** in a dichloromethane/methanol mixture. Characterization of **1**, **2**, and **4** by X-ray crystallography confirms the 2:3 gold/ligand ratio of all three complexes. The coordination polymer **1** maintains a high degree of solvation in the solid-state with three chloroform adducts hydrogen-bonded to the chloride ligand on each gold atom. These chloroform molecules are sandwiched between the two-dimensional polymeric sheets of **1**. The crystal structure of **4** reveals an empty, iodide-capped metallocryptand cage with the tetrahedrally distorted gold atoms and the nitrogen atoms on the pyridazine rings directed away from the center of the cavity. No metal ion encapsulation was observed for complex **4**. Complex **2** forms one-dimensional arrays of [Au<sub>2</sub>(P<sub>2</sub>pz)<sub>2</sub>]<sup>2+</sup> metallomacrocycles connected to each other by a third P<sub>2</sub>pz ligand. The electronic absorption spectra (CH<sub>2</sub>Cl<sub>2</sub>) of **1**–**4** show broad, nearly featureless absorption bands that tail into the visible with  $\pi$ – $\pi^*$  bands at 296 nm and discernible shoulders at 314 nm for **2** and 334 nm for **3**. Excitation into the low energy band of **2** produces only a modest emission in solution at 540 nm ( $\lambda_{\text{ex}}$  468 nm) and 493 nm ( $\lambda_{\text{ex}}$  403 nm). Under identical conditions, the P<sub>2</sub>pz ligand also emits at 540 and 493 nm.

### Introduction

The investigation of interactions between closed-shell, heavy metal ions or atoms continues to attract attention.<sup>1</sup> Employing multidentate ligands with specific geometric arrangements and an affinity toward metal ions or atoms is one approach to induce metal–metal interactions, and numerous examples of extended arrays of multimetallic complexes have been produced.<sup>2</sup> Alternatively, it is possible to induce short metal–metal interactions through the encapsulation of metal ions into the center of a metallocryptand. Che

and co-workers<sup>3</sup> first used this approach in 1994 to successfully bind a potassium ion into the center of the [Au<sub>2</sub>(P<sub>2</sub>nap)<sub>3</sub>]<sup>2+</sup> metallocryptand cage (P<sub>2</sub>nap is 2,7-bis(diphenylphosphino)-1,8-naphthyridine). We too, have been interested in the metal–metal interaction found within metallocryptand cages (Scheme 1).<sup>4</sup> By changing the ligand backbone of the metallocryptand, the internal cavity is altered, and therefore, the intermetallic separations can be varied. Toward this endeavor, a variety of multidentate phosphine ligands have been employed including P<sub>2</sub>phen, P<sub>2</sub>bpy, and

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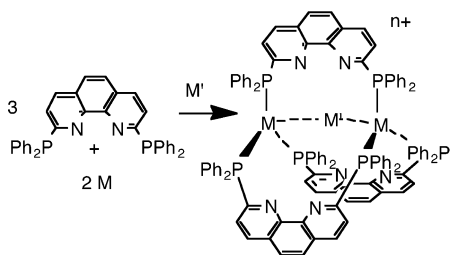
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Scheme 1



$P_2nap$  where  $P_2phen$  is 2,9-bis(diphenylphosphino)-1,10-phenanthroline and  $P_2bpy$  is 6,6'-bis(diphenylphosphino)-2,2'-bipyridine.<sup>4</sup> During these studies, we have never observed polymer formation even though there are numerous examples of coordination polymers using late transition metals and multidentate ligands.<sup>5</sup>

The importance of metal containing polymers for new materials is quite extensive,<sup>6</sup> and Au(I) based polymers are of particular importance due to their unique photophysical properties.<sup>7,8</sup> Often complexes with inter- or intramolecular Au(I)···Au(I) interactions are intensely luminescent, and perturbations of these interactions can form the basis of a luminescent sensor.<sup>9</sup> The ability to form polymeric complexes is often dictated by the geometry of the multidentate ligand. A large number of ligands, particularly multidentate phosphine ligands, have been designed to hold gold atoms in close proximity to each other. Because gold(I) complexes are known to adopt a variety of coordination modes, including two-, three-, or four-coordinate, it was of interest to see if the tetradentate  $P_2pz$  ligand ( $P_2pz$  is 3,6-bis(diphenylphos-

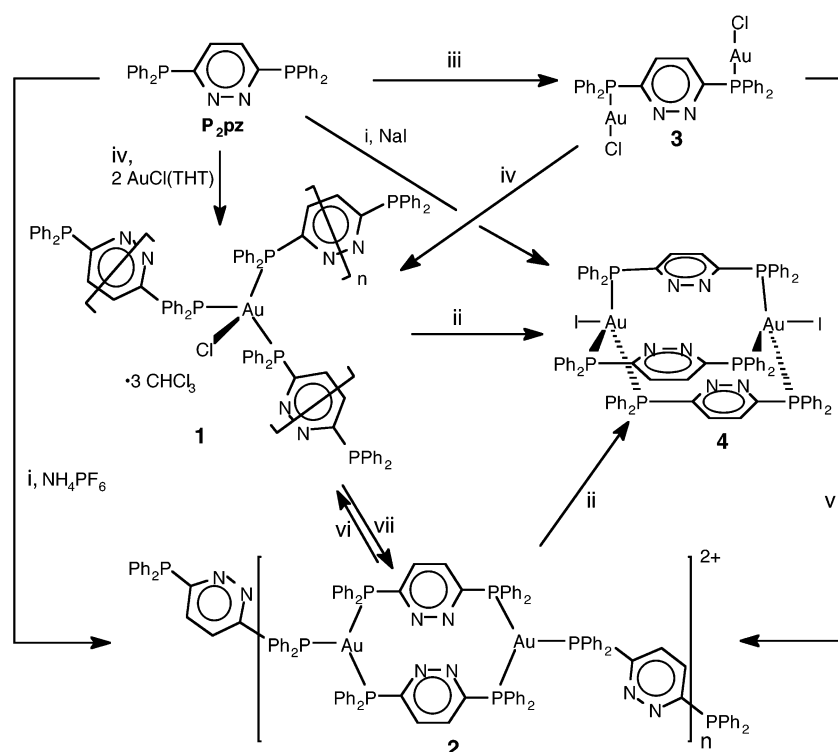
phino)pyridazine) would coordinate to gold(I) in a polymeric fashion or whether it would form a metallocryptand. Interestingly, it does both, and here we report the formation of two polymeric complexes of Au(I), their interconversion, and their conversion to an empty metallocryptand.

## Results

According to Scheme 2, the two-dimensional polymer  $\{Au_2Cl_2(P_2pz)_3\}_n$ , **1**·6CHCl<sub>3</sub>, was prepared by reacting 1 equiv of AuCl(tht) (tht is tetrahydrothiophene) with 1.5 equiv of  $P_2pz$  in chloroform giving a pale yellow solution. Also seen in Scheme 2 is the one-dimensional polymeric complex  $\{[Au_2(P_2pz)_3](PF_6)_2\}_n$ , **2**, prepared by reacting **1** with excess  $NH_4PF_6$  in a 1:1 dichloromethane/methanol mixture. The simple digold complex  $(AuCl)_2(P_2pz)$ , **3**, is formed by the reaction of 2 equiv of AuCl(tht) with 1 equiv of  $P_2pz$  giving rise to a sharp singlet in the  $^{31}P\{^1H\}$  NMR spectrum at 33.0 ppm. Additionally, **1** can be formed by the reaction of **3** with 2 equiv of  $P_2pz$  in chloroform or by the reaction of **2** with  $Et_4NCl$  in chloroform. All reactions to form **1** produce  $^{31}P\{^1H\}$  NMR spectra that show a broad resonance at 23.6 ppm, indicative of a dynamic process, and two smaller resonances at 20.2 and 19.8 ppm, identified as the diphosphine oxide and monophosphine oxide comprising only 5% of the total spectrum. Moreover, the macrocyclic polymer, **2**, may be formed by reacting **3** with  $NH_4PF_6$  and 2 equiv of  $P_2pz$  in a dichloromethane/methanol mixture or directly by reacting 1 equiv of AuCl(tht) with 1.5 equiv of  $P_2pz$  with excess  $NH_4PF_6$  in the same solvent. Similar to the formation of **1**, reactions to form **2** also give rise to a broad  $^{31}P\{^1H\}$  NMR resonance indicative of a dynamic process (41.1 ppm for the phosphorus atoms of the  $P_2pz$  ligand and a heptet at  $-142.7$  ppm for the phosphorus atom of the  $PF_6^-$  anion ( $^1J_{F-P} = 704$  Hz)). Further, the empty metallocryptand complex  $Au_2I_2(P_2pz)_3$ , **4**, can also be produced by a variety of methods as shown in Scheme 2. Complex **4** forms by reacting **2** with excess NaI in a 2:1 dichloromethane/methanol mixture, reacting **1** with excess NaI also in a dichloromethane/methanol mixture, or by reacting **3** with 2 equiv of AuCl(tht) and excess NaI. All of these reactions give rise to a variety of resonances in the  $^{31}P\{^1H\}$  NMR spectrum with the largest resonance (comprising 95% of the spectrum) at 15.3 ppm. Once crystallized, compound **4** is insoluble in common organic solvents including dimethyl sulfoxide, acetone, acetonitrile, dichloromethane, chloroform, and methanol, and  $^{31}P\{^1H\}$  NMR spectra could not be obtained on the isolated product.

As indicated by the broad  $^{31}P\{^1H\}$  NMR resonances, the polymeric complexes **1** and **2** are dynamic in solution and freely exchange ligand. This exchange process was explored by  $^{31}P\{^1H\}$  NMR spectroscopy by successive additions of  $P_2pz$  to AuCl(tht). Addition of  $1/2$  equiv of  $P_2pz$  to 1 equiv of AuCl(tht) produces a single sharp resonance at 33.0 ppm that is attributed to the formation of  $Au_2Cl_2(P_2pz)$ , **3**. Addition of a second  $1/2$  equiv of  $P_2pz$  causes the sharp resonance at 33.0 ppm to broaden slightly and diminish in intensity while two other broad resonances are seen at 24.0 and 23.6 ppm. Addition of yet another  $1/2$  equiv of  $P_2pz$  significantly

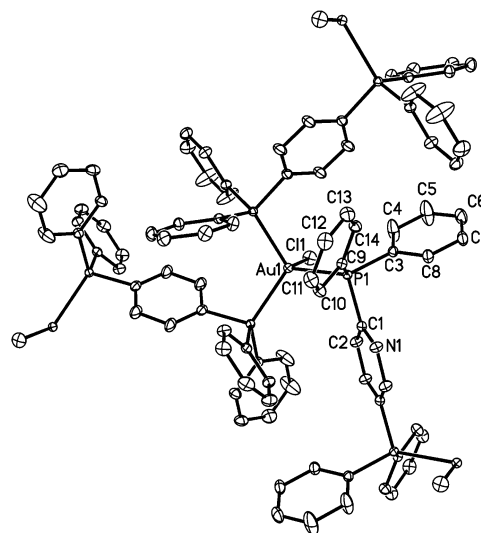
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Scheme 2<sup>a</sup>

<sup>a</sup> (i)  $2/3$  AuCl(tht),  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ ; (ii) NaI,  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ ; (iii) 2AuCl(tht),  $\text{CH}_2\text{Cl}_2$ ; (iv) 2P<sub>2</sub>pz,  $\text{CHCl}_3$ ; (v) 2P<sub>2</sub>pz,  $\text{NH}_4\text{PF}_6$ ,  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ ; (vi)  $\text{Et}_4\text{Cl}$ ,  $\text{CHCl}_3$ ; (vii)  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ ,  $\text{NH}_4\text{PF}_6$ .

simplifies the spectrum resulting in a broad resonance at 23.6 ppm assigned to complex **1** (comprising the majority of the spectrum), along with two smaller sharp singlets, associated with the mono- and diphosphine oxides. Subsequent additions of  $1/2$  equiv of P<sub>2</sub>pz move the large broad resonance further upfield toward that of the free ligand. No resonance was observed for free ligand throughout the experiment, indicating that the ligand and the metal complex are involved in a fast exchange process. Attempts to obtain low temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy data were thwarted by precipitation of products from their corresponding solutions upon cooling.

Crystals of **1** suitable for X-ray analysis formed upon standing from a chloroform solution of **1**. The complex crystallizes in the rhombohedral space group  $R\bar{3}$  with the AuCl unit oriented on a crystallographic 3-fold axis. Thus, only one-third of the Au(I) coordination environment is unique. A thermal ellipsoid drawing of **1** is shown in Figure 1 while selected bond distances and angles are presented in Table 1. In complex **1**, each gold(I) atom resides in a distorted tetrahedral environment and is bound to three phosphorus atoms of three separate P<sub>2</sub>pz ligands and to one chloride ligand. Because of the crystallographic symmetry, the three Au–P distances of **1** are identical at 2.3683(6) Å. These values are slightly shorter than those found in the solvate-free, distorted tetrahedral AuCl(PPh<sub>3</sub>)<sub>3</sub> complex reported by Jones et al.,<sup>10</sup> where the shortest Au–P distance is 2.395(2) Å, and are closer to the values (2.3666(6)–

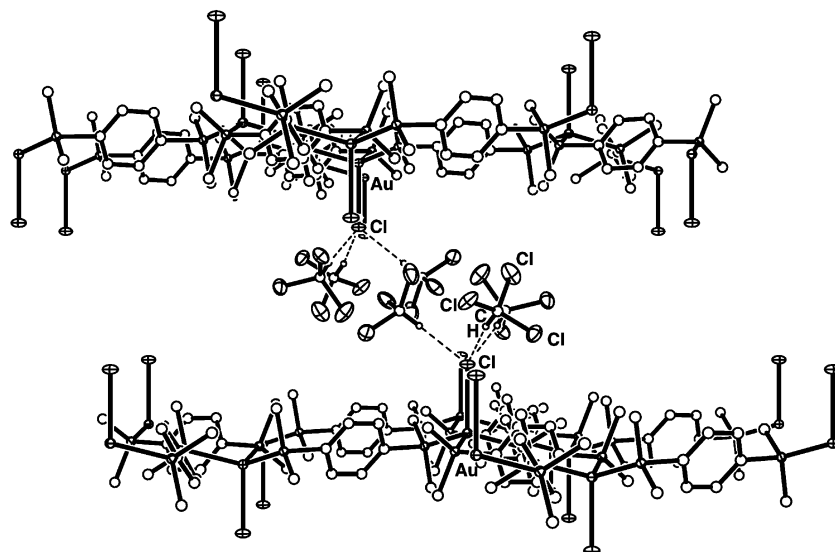


**Figure 1.** Thermal ellipsoid plot of **1** with hydrogen atoms omitted for clarity. Only the asymmetric unit is numbered. The asymmetric unit contains one-third of a Au–Cl unit and three-halves of a P<sub>2</sub>pz ligand.

2.3911(6) Å) found in the bis(solvate) form, AuCl(PPh<sub>3</sub>)<sub>3</sub>·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub>, reported by Schmidbaur and co-workers.<sup>11</sup> However, the Au–Cl distance in **1** (2.7026(10) Å) shows the opposite trend and is closer to the separation found in solvent-free form of AuCl(PPh<sub>3</sub>)<sub>3</sub> (2.710(2) Å) than the corresponding separation in AuCl(PPh<sub>3</sub>)<sub>3</sub>·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub> (2.7962(6) Å). The deviation from tetrahedral geometry can be seen in the P–Au–P angles which are identical at 113.779(10)°

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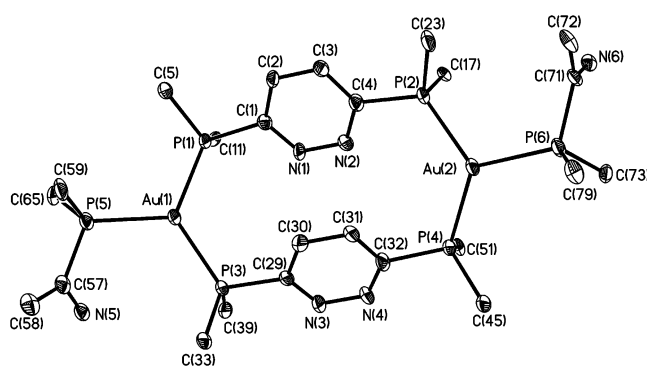
**Figure 2.** Structural drawing emphasizing the two-dimensional polymeric sheets of **1**. The alternating “up and down” orientations of the Au–Cl units in the polymer are shown along with the three chloroform solvate molecules per Au–Cl unit.

**Table 1.** Bond Lengths (Å) and Angles (deg) for **1**

|                   |             |
|-------------------|-------------|
| Au(1)–P(1)        | 2.3683(6)   |
| Au(1)–Cl(1)       | 2.7026(10)  |
| P(1)–C(1)         | 1.826(2)    |
| P(1)–C(3)         | 1.821(2)    |
| P(1)–C(9)         | 1.811(2)    |
| Au···Au           | 8.893       |
| P(1)–Au(1)–P(1)#1 | 113.779(10) |
| Au(1)–P(1)–C(9)   | 111.08(7)   |
| Au(1)–P(1)–C(3)   | 125.09(7)   |
| Au(1)–P(1)–C(1)   | 108.18(7)   |
| C(1)–P(1)–C(3)    | 100.79(9)   |
| C(1)–P(1)–C(9)    | 104.89(10)  |
| C(3)–P(1)–C(9)    | 104.79(9)   |

while the P–Au–Cl angles are  $104.715(12)^\circ$ . The Au(I) center resides out of the plane formed by the three phosphorus atoms toward the  $\text{Cl}^-$  ligand by  $0.6015 \text{ \AA}$ . Complex **1** shows no close Au···Au interactions, and the closest Au···Au separation ( $8.893 \text{ \AA}$ ) is between Au(I) atoms in the same two-dimensional sheet. As shown in Figure 2, the AuCl units alternate their orientation to each side of the polymeric plane. Compound **1** shows a high degree of solvation in the crystal structure with three chloroform solvates hydrogen bonded to the chloride ligand of each gold atom. These chloroform molecules are sandwiched between the polymer sheets of **1** and comprise  $\sim 30\%$  by mass of this polymer.

Crystals of **2** suitable for X-ray diffraction analysis were grown by the slow diffusion of benzene into a saturated 1,2-dichloroethane solution of **2**. The one-dimensional polymer crystallizes in the triclinic space group  $P\bar{1}$ . Figure 3 shows a thermal ellipsoid drawing of **2** with selected bond distances and angles presented in Table 2. Complex **2** forms one-dimensional arrays of  $[\text{Au}_2(\text{P}_2\text{pz})_2]^{2+}$  metallomacrocycles connected to each other by a third  $\text{P}_2\text{pz}$  ligand as presented in Figure 4. The closest Au···Au separation is long at  $8.268 \text{ \AA}$ . The three-coordinate Au(1) center is nearly planar with combined angles about the Au(1) center totaling  $359.75^\circ$ . The Au atom is displaced out of its phosphorus plane by only  $0.0687 \text{ \AA}$ . The P(1)–Au(1)–P(3), P(1)–Au(1)–P(5), and P(3)–Au(1)–P(5) angles are  $124.48(7)^\circ$ ,  $114.77(7)^\circ$ , and

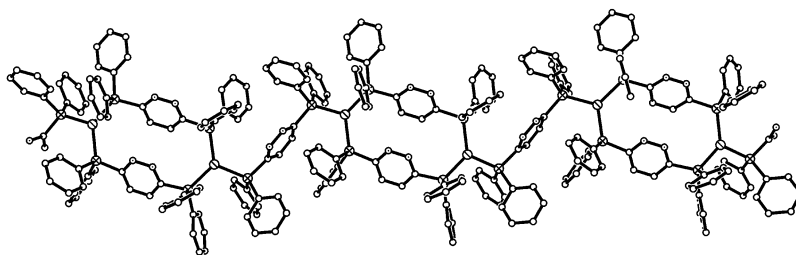


**Figure 3.** X-ray structural drawing of cationic portion of **2** showing only one unit of the repeating polymeric structure with all but the ipso carbon atom of the phenyl rings and hydrogen atoms omitted for clarity.

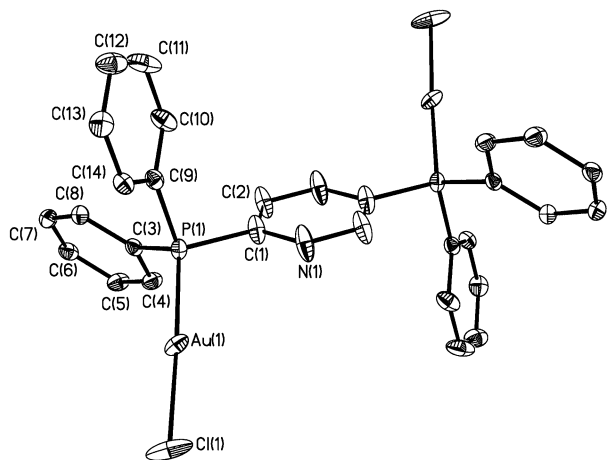
**Table 2.** Bond Lengths (Å) and Angles (deg) for **2**

|                  |            |
|------------------|------------|
| Au(1)–P(1)       | 2.363(2)   |
| Au(1)–P(3)       | 2.347(2)   |
| Au(1)–P(5)       | 2.380(2)   |
| Au(2)–P(2)       | 2.369(2)   |
| Au(2)–P(4)       | 2.342(2)   |
| Au(2)–P(6)       | 2.3709(19) |
| Au···Au          | 8.268      |
| P(1)–Au(1)–P(3)  | 124.48(7)  |
| P(1)–Au(1)–P(5)  | 114.77(7)  |
| P(3)–Au(1)–P(5)  | 120.50(7)  |
| P(2)–Au(2)–P(4)  | 123.23(7)  |
| P(2)–Au(2)–P(6)  | 114.18(7)  |
| P(4)–Au(2)–P(6)  | 121.50(7)  |
| Au(1)–P(1)–C(1)  | 117.2(2)   |
| Au(1)–P(3)–C(29) | 114.9(2)   |
| Au(2)–P(2)–C(4)  | 119.8(3)   |
| Au(2)–P(4)–C(32) | 114.5(3)   |

$120.50(7)^\circ$ , respectively, with the largest angle corresponding to the internal angle of the gold macrocycle. The three-coordinate Au(2) center is slightly less planar and is displaced out of its phosphorus plane by  $0.1422 \text{ \AA}$ . The sum of the angles around Au(2) total  $358.91^\circ$ . Similar to the angles around Au(1), the P(2)–Au(2)–P(4), P(2)–Au(2)–P(6), and P(4)–Au(2)–P(6) angles are  $123.23(7)^\circ$ ,  $114.18(7)^\circ$ , and  $121.50(7)^\circ$ , respectively, with the largest angle again corre-



**Figure 4.** Structural drawing of cationic portion of **2** emphasizing the polymeric nature of the complex. Each gold atom adopts a nearly trigonal planar coordination environment with the gold atoms forming a “zigzag” pattern.



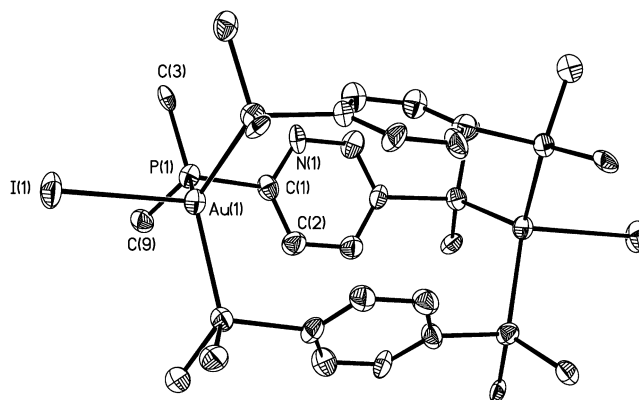
**Figure 5.** X-ray structural drawing of **3** looking down at the pyridazine ring.

**Table 3.** Bond Lengths (Å) and Angles (deg) for **3**

|                  |            |
|------------------|------------|
| Au(1)–P(1)       | 2.2263(10) |
| Au(1)–Cl(1)      | 2.2852(12) |
| P(1)–C(1)        | 1.825(4)   |
| P(1)–C(3)        | 1.805(4)   |
| P(1)–C(9)        | 1.811(4)   |
| Au $\cdots$ Au   | 3.570      |
|                  |            |
| P(1)–Au(1)–Cl(1) | 177.58(5)  |
| Au(1)–P(1)–C(1)  | 111.10(17) |
| Au(1)–P(1)–C(3)  | 112.87(12) |
| Au(1)–P(1)–C(9)  | 117.74(13) |
| C(1)–P(1)–C(3)   | 105.59(18) |
| C(1)–P(1)–C(9)   | 103.26(19) |
| C(3)–P(1)–C(9)   | 105.18(18) |

sponding to the internal angle of the gold macrocycle. The Au–P separations in **2** range from 2.342(2) to 2.380(2) Å and are slightly shorter than those observed in **1**.

X-ray quality crystals of complex **3** were formed by the slow diffusion of *tert*-butylmethyl ether into a chloroform solution of **3**. A thermal ellipsoid plot of **3** is presented in Figure 5 with selected bond distances and angles in Table 3. The nearly colorless complex crystallizes in the monoclinic space group *C2/c* with the middle of the pyridazine ring residing on a crystallographic inversion center making only one-half of the complex crystallographically unique. The nearest intermolecular Au $\cdots$ Au separation is 3.570 Å and is considered only very weakly aurophilic.<sup>12</sup> As in many other structures containing Au $\cdots$ Au interactions, the two intermolecular P–Au–Cl subunits are oriented nearly orthogonal to each other. The intermolecular P–Au $\cdots$ Au–P torsion angle is 110.7°. The two-coordinate Au(I) atoms are nearly linear with the angle P(1)–Au(1)–Cl(1) of 177.58(5)° and



**Figure 6.** Thermal ellipsoid plot of **4** with hydrogen atoms and all but the ipso carbon atoms on the phenyl rings omitted for clarity.

Au(1)–P(1) and Au(1)–Cl(1) separations of 2.2263(10) and 2.2852(12) Å, respectively. The Au(1)–P(1)–C(1), Au(1)–P(1)–C(3), and Au(1)–P(1)–C(9) angles are slightly expanded from the ideal tetrahedral angles (109.5°) at 110.10(17)°, 112.87(12)°, and 117.74(13)°, respectively.

Yellow crystals of **4** were obtained by the slow diffusion of diethyl ether into a dichloromethane solution of **4**. Once crystallized, complex **4** is no longer soluble in common organic solvents. Complex **4** crystallizes in the hexagonal *P6(3)/m* space group with the gold atom on a crystallographic screw axis with only one-sixth of the molecule being crystallographically unique. A thermal ellipsoid plot of **4** is shown in Figure 6 with selected bond distances and angles presented in Table 4. The structure shows an empty metallocryptand cage capped by two iodine atoms and two gold atoms triply bridged by the P<sub>2</sub>pz ligand. The gold atoms reside in distorted tetrahedral coordination environments with P–Au–P and P–Au–I angles of 115.37(7)° and 102.62(9)°, respectively. The Au(1)–I(1) separation is 2.8726(19) Å, and the Au–P separations are longer than those observed in **1–3** at 2.417(4) Å. The nitrogen atoms in the pyridazine rings are oriented slightly away from the cavity of the metallocryptand cage preventing the nitrogen atom lone pairs from penetrating the cage. The Au(I) atoms in **4** pucker away from the cavity of the metallocryptand cage by 0.5280 Å,

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**Table 4.** Bond Lengths (Å) and Angles (deg) for **4**

|                 |            |
|-----------------|------------|
| Au(1)–P(1)      | 2.417(4)   |
| Au(1)–I(1)      | 2.8726(19) |
| P(1)–C(1)       | 1.855(14)  |
| P(1)–C(3)       | 1.806(14)  |
| P(1)–C(9)       | 1.781(14)  |
| Au···Au         | 7.373      |
|                 |            |
| P(1)–Au(1)–I(1) | 102.62(9)  |
| Au(1)–P(1)–C(1) | 107.5(5)   |
| Au(1)–P(1)–C(3) | 117.4(5)   |
| Au(1)–P(1)–C(9) | 119.8(5)   |
| C(1)–P(1)–C(3)  | 105.8(6)   |
| C(1)–P(1)–C(9)  | 103.3(7)   |
| C(3)–P(1)–C(9)  | 101.5(6)   |

and the intramolecular Au···Au separation is long at 7.373 Å. Attempts to incarcerate Na<sup>+</sup>, Tl<sup>+</sup>, Pb<sup>2+</sup>, or Hg(0) into the empty cage of **4** proved unsuccessful.

The electronic absorption spectra (CH<sub>2</sub>Cl<sub>2</sub>) of **1–4** show broad, nearly featureless absorption bands that tail into the visible with  $\pi$  to  $\pi^*$  bands at 296 nm and discernible shoulders at 314 nm for **2** and 334 nm for **3**. Excitation into the low energy band of **2** produces only a modest emission in solution at 540 nm ( $\lambda_{\text{ex}}$  468 nm) and 493 nm ( $\lambda_{\text{ex}}$  403 nm). Under identical conditions, the P<sub>2</sub>pz ligand also emits at 540 and 493 nm. In the gas phase, the polymeric complexes disintegrate into their respective components, and no fragment larger than [Au<sub>2</sub>(P<sub>2</sub>pz)<sub>2</sub>]<sup>2+</sup> could be identified.

## Experimental Section

All solvents were purified with a Grubbs apparatus.<sup>13</sup> P<sub>2</sub>pz<sup>3</sup> and AuCl(tht)<sup>14</sup> were prepared from literature procedures. <sup>1</sup>H chemical shifts are reported relative to TMS, and <sup>31</sup>P{<sup>1</sup>H} chemical shifts are reported relative to 85% H<sub>3</sub>PO<sub>4</sub>. Combustion analysis was performed by Desert Analytics, Tucson, AZ. UV–vis spectra were obtained using a Hewlett-Packard 8453 diode array spectrometer (1 cm path-length cells). Emission data were recorded using a Spex Fluoromax steady-state fluorimeter.

**Preparation of {Au<sub>2</sub>Cl<sub>2</sub>(P<sub>2</sub>pz)<sub>3</sub>·6CHCl<sub>3</sub>}<sub>n</sub>, **1**·6CHCl<sub>3</sub>.** A 25 mL Erlenmeyer flask was charged with 0.167 g (0.520 mmol) of AuCl(tht) in 5 mL of dichloromethane followed by 0.350 g (0.780 mmol) of P<sub>2</sub>pz in 5 mL of dichloromethane. After stirring for 15 min, a white precipitate formed. At this point, 1.5 mL of methanol was added dissolving the precipitate. This mixture was then stirred for 2 h forming a yellow solution. The solvent was removed by rotary evaporation, and the remaining yellow solid was redissolved in chloroform and filtered through Celite. Pale yellow crystals of **1** (0.363 g, 0.401 mmol) precipitated from the chloroform solution upon standing overnight (77%). Elemental Anal. Calcd (C<sub>90</sub>H<sub>72</sub>·Au<sub>2</sub>Cl<sub>20</sub>N<sub>6</sub>P<sub>6</sub>): C, 42.78; H, 2.87; N, 3.33. Found: C, 42.72; H, 2.91; N, 3.33. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.52 (m), 7.30 (m), 7.14 (m). <sup>31</sup>P{<sup>1</sup>H} NMR (202.33 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 23.6 (broad).

**Preparation of {[Au<sub>2</sub>(P<sub>2</sub>pz)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>]<sub>n</sub>, **2**.** A 25 mL Erlenmeyer flask was charged with 0.317 g (0.350 mmol) of **1**. To this was added 0.570 g (3.50 mmol) of NH<sub>4</sub>PF<sub>6</sub> in 5 mL of methanol. This mixture was allowed to stir for 30 min after which the volatiles were removed using a rotary evaporator. The remaining yellow white solid was dissolved in 25 mL of dichloromethane and filtered through Celite leaving a yellow solution. The volatiles

were then removed by rotary evaporation leaving 0.318 g (0.313 mmol) of **2** as a yellow solid (90%). Elemental Anal. Calcd (C<sub>84</sub>H<sub>66</sub>Au<sub>2</sub>F<sub>12</sub>N<sub>6</sub>P<sub>8</sub>): C, 49.72; H, 3.28; N, 4.14. Found: C, 49.72; H, 3.48; N, 4.19. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  = 9.35 (m), 9.25 (m), 9.13 (m). <sup>31</sup>P{<sup>1</sup>H} NMR (202.33 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  = 41.1 (broad), –142.7 (hept, <sup>1</sup>J<sub>F–P</sub> = 704 Hz).

**Preparation of (AuCl)<sub>2</sub>(P<sub>2</sub>pz), **3**.** A 25 mL Erlenmeyer flask was charged with 10 mL of dichloromethane, 0.055 g of P<sub>2</sub>pz (0.122 mmol), and 0.081 g (0.252 mmol) of AuCl(tht). This mixture was stirred for 2 h after which the solvent was removed by rotary evaporation. The remaining tan solid was dissolved in a minimum amount of dichloromethane and precipitated with diethyl ether to afford 0.082 g (0.090 mmol) of **3** as a tan solid (73%). This solid is easily crystallized by dissolving in a small volume of chloroform (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, or 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) followed by precipitation with diethyl ether. Elemental Anal. Calcd (C<sub>28</sub>H<sub>22</sub>Au<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>·1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>): C, 35.60; H, 2.59; N, 2.77. Found: C, 35.70; H, 2.30; N, 2.94. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.90 (m), 7.65 (m), 7.46 (m). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 33.0 (s).

**Preparation of Au<sub>2</sub>I<sub>2</sub>(P<sub>2</sub>pz)<sub>3</sub>, **4**.** A 25 mL Erlenmeyer flask was charged with 0.141 g (0.139 mmol) of **2** and 10 mL of dichloromethane. To this was added 0.208 g (1.39 mmol) of NaI in 5 mL of methanol. This mixture was stirred overnight, after which the mixture was filtered through Celite, and the remaining yellow solution was evaporated to dryness. The remaining yellowish solid was dissolved in dichloromethane and filtered through Celite. The remaining yellow solution was evaporated to dryness leaving 0.182 g (0.091 mmol) of **4** as a yellow solid (65%). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>OD, 25 °C):  $\delta$  = 15.3 (broad).

**X-ray Crystallography.** Crystal data for **1–4** are presented in Table 5. Suitable crystals of **1**, **2**, and **3** were coated with light petroleum oil, mounted on a glass fiber, and placed in the 91 K nitrogen cold stream of a Siemens SMART diffractometer while a suitable crystal of **4** was coated with epoxy cement and mounted on a Siemens P4 diffractometer. Unit cell parameters were determined by least-squares analysis of 712 reflections for **1**, 972 reflections for **2**, and 940 reflections for **3**. For **4**, unit cell parameters were determined by least-squares analysis of 25 reflections with 3.45° <  $\theta$  < 12.35°. A total of 10211 reflections were collected in the range 1.9° <  $\theta$  < 31.5°, yielding 5250 unique reflections ( $R_{\text{int}}$  = 0.008) for **1**, while a total of 21205 reflections were collected in the range 1.42° <  $\theta$  < 27.5°, yielding 14331 unique reflections ( $R_{\text{int}}$  = 0.053) for **2**, and a total of 17523 reflections were collected in the range 1.9° <  $\theta$  < 31.5°, yielding 4292 unique reflections ( $R_{\text{int}}$  = 0.032) for **3**. For **4**, a total of 7120 reflections in the range 1.9° <  $\theta$  < 25° were collected yielding 2855 unique data ( $R_{\text{int}}$  = 0.11). The data were corrected for absorption and Lorentz and polarization effects. Scattering factors and corrections for anomalous dispersion were taken from a standard source.<sup>15</sup>

Calculations were performed using the Siemens SHELXTL Version 5.10 system of programs refining on  $F^2$ . The structures were solved by direct methods. In complexes **1** and **3**, the pyridazine ring incorporates a crystallographic symmetry element rendering the carbon and nitrogen atoms attached to the ipso carbon atom equivalent. These two positions are indistinguishable and therefore modeled as 50% nitrogen and 50% carbon each. In **2** and **4**, the nitrogen atom positions were determined by inspection and comparison of the respective anisotropic thermal parameters.

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Table 5. Crystallographic Data for 1–4

|  | 1·6CHCl <sub>3</sub>   | 2·2.25C <sub>6</sub> H <sub>6</sub> ·<br>0.75(1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )              | 3   | 4·CH <sub>2</sub> Cl <sub>2</sub>  |
|--|--|--|---|--|
| formula                                | C <sub>90</sub> H <sub>72</sub> Au <sub>2</sub> Cl <sub>20</sub> N <sub>6</sub> P <sub>6</sub> | C <sub>101</sub> H <sub>85</sub> Au <sub>2</sub> Cl <sub>2</sub> F <sub>12</sub> N <sub>6</sub> P <sub>8</sub> | C <sub>28</sub> H <sub>20</sub> Au <sub>2</sub> Cl <sub>2</sub> N <sub>2</sub> P <sub>2</sub> | C <sub>85</sub> H <sub>66</sub> Au <sub>2</sub> Cl <sub>2</sub> I <sub>2</sub> N <sub>6</sub> P <sub>6</sub> |
| fw                                     | 420.04   | 2251.42  | 911.23  | 2075.89  |
| a, Å                                   | 15.253(2)  | 16.233(2)  | 17.2902(13)   | 13.6458(12)  |
| b, Å                                   | 15.253(2)  | 16.303(2)  | 13.3536(9)  | 13.6458(12)  |
| c, Å                                   | 36.565(7)  | 20.110(3)  | 11.7382(9)  | 29.446(6)  |
| α, deg                                 | 90   | 95.600(4)  | 90  | 90   |
| β, deg                                 | 90   | 102.745(3)   | 103.322(3)  | 90   |
| γ, deg                                 | 120  | 112.860(2)   | 90  | 120  |
| V, Å <sup>3</sup>                      | 7368(2)  | 4682.5(11)   | 2637.3(3)   | 4748.5(11)   |
| space group                            | R $\bar{3}$  | P $\bar{1}$  | C2/c  | P6 <sub>3</sub> /m   |
| Z                                      | 18   | 2  | 4   | 2  |
| D <sub>calcd</sub> , g/cm <sup>3</sup> | 1.704  | 1.597  | 2.295   | 1.452  |
| crystal size, mm <sup>3</sup>          | 0.30 × 0.22 × 0.21   | 0.24 × 0.20 × 0.10   | 0.14 × 0.18 × 0.08  | 0.14 × 0.42 × 0.44   |
| μ (Mo Kα), mm <sup>-1</sup>            | 3.673  | 3.383  | 3.934   | 11.459   |
| λ, Å                                   | 0.71073  | 0.71073  | 0.71073   | 0.71073  |
| temp, K                                | 91(2)  | 91(2)  | 91(2)   | 298(2)   |
| transm factors                         | 0.40–0.51  | 0.50–0.73  | 0.23–0.46   | 0.53–0.95  |
| R1, wR2 (I ≥ σ(I))                     | 0.0243, 0.0604   | 0.0523, 0.1342   | 0.0269, 0.0616  | 0.0706, 0.1742   |

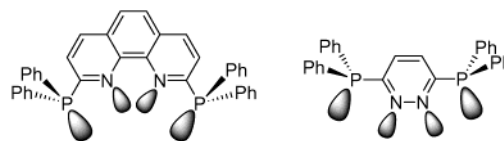
Complex **2** contains two and one-quarter benzene solvates and three-fourths of a dichloroethane solvate straddling a symmetry element. In **4**, the unit cell contains a slightly disordered dichloromethane solvate. There are no unusual contacts between any of these moieties, and simple models of the disorder provided satisfactory refinements.

## Discussion

The coordination chemistry of P<sub>2</sub>pz is relatively unexplored with only four other reports<sup>16–19</sup> of this ligand. A silver(I) metallocryptand, similar to **4**, was recently reported in which the five-coordinate silver(I) atoms are capped by nitrate anions and coordinated to three bridging P<sub>2</sub>pz ligands.<sup>18</sup> Although Ag(I) has a tendency to adopt a linear two-coordinate geometry, multiple coordination modes are not uncommon, and the metallocryptand structural motif has been observed in other silver(I) complexes utilizing P<sub>2</sub>phen<sup>4e</sup> or bis(diphenylphosphino)acetylene as the triply bridging ligand backbone and either triflate or nitrate anions as capping molecules.<sup>19</sup> Complex **4** is less elongated than the aforementioned silver(I) complex.<sup>18</sup> The nearest Au···Au separation is through the empty cage at 7.373 Å, while the corresponding Ag···Ag separation, also through the empty cage, is longer at 7.543 Å. This increased elongation of the silver(I) cage complex also results in an increased puckering of the metal atoms away from the phosphine plane. The gold atoms in **4** are only 0.5280 Å out of the phosphine plane while in the analogous silver(I) complex they are 0.673 and 0.646 Å.<sup>18</sup> Additionally, a polymeric complex containing Ag(I) and P<sub>2</sub>pz has been reported.<sup>7</sup> It should not be surprising that the Au(I) analogue also forms polymers. However, it is somewhat unusual to find multiple structural motifs for the same stoichiometric composition as illustrated by the isolation of the one- and two-dimensional polymers along with

the empty metallocryptand cage complex, all of which have a Au/P<sub>2</sub>pz ratio of 2:3. Interestingly, once the empty cage complex forms, the dynamic nature of the gold–phosphine coordination is stopped suggesting that the polymeric complexes are the kinetic products while the cage complex is the thermodynamic product.

In previous studies with P<sub>2</sub>phen, there was a noticeable lack of polymer formation. This may be due, in part, to the rapid uptake of a guest metal ion which appears to “turn-off” ligand substitution around the three-coordinate Au(I) center. For example, the addition of excess Na<sup>+</sup> to Au(I) and P<sub>2</sub>phen produces the Na<sup>+</sup> encapsulated metallocryptand, [Au<sub>2</sub>Na(P<sub>2</sub>phen)<sub>3</sub>]<sup>+</sup>, but in the reaction of Au(I), Na<sup>+</sup>, and P<sub>2</sub>pz no encapsulation was observed.<sup>4d</sup> This is peculiar because the lone pairs of electrons on the nitrogen atoms in P<sub>2</sub>phen do not participate in the binding of Na<sup>+</sup> ion in [Au<sub>2</sub>Na(P<sub>2</sub>phen)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>,<sup>4d</sup> however, in the P<sub>2</sub>nap analogue, [Au<sub>2</sub>Na(P<sub>2</sub>nap)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>,<sup>4e</sup> the lone pair of electrons on the nitrogen atoms is essential for Na<sup>+</sup> binding to occur. In both



cases, no polymer formation occurred, although in the former the system is dynamic and exists as an equilibrium mixture of the coordinated metallocryptate, empty metallocryptand, and metallomacrocyclic with two ligands. In the case of P<sub>2</sub>pz, the lone pair of electrons on the nitrogen atoms could provide a template for a guest metal coordination, yet no binding of metal ions was observed. Attempts to add aurophilic metal ions or metals (Tl<sup>+</sup>, Hg(0)) that are known to bind to Au(I) centers in the absence of stabilizing ligand interactions<sup>4a,d</sup> also failed. One explanation for this behavior may be related to the relative positions of the phosphorus lone pairs of electrons on P<sub>2</sub>pz versus P<sub>2</sub>phen or P<sub>2</sub>nap. Their outward orientation would seem to prohibit small-cage formation. The metallocryptand formed with P<sub>2</sub>pz has Au···Au separations that are far too large to

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facilitate guest binding, and the filled  $d_{z^2}$  orbital of the gold(I) atoms cannot effectively penetrate the cavity to help immobilize a metal or metal ion within the cage through noncovalent interactions. Furthermore, the internal lone pairs on the nitrogen atoms of  $P_2pz$  are also outwardly directed, significantly reducing their ability to stabilize an incarcerated metal ion. It is interesting to speculate whether there is enough flexibility in the P–C bond to distort the Au(I)– $P_2pz$  coordination environment enough to allow guest binding. Molecular modeling suggests that in the absence of an axial ligands ( $I^-$  in the case of **4**) simple twisting of the trigonally coordinated  $[AuP_3]^+$ -centers relative to each other significantly reduces the Au···Au separation and provides a means to form a suitably sized metallocryptand to encapsulate a metal or metal ion. As demonstrated by the successful preparation of metallocryptands using  $P_2bpy$  and  $P_2phen$ , the

interaction of the nitrogen lone pairs with the guest metal is not critical, and the outward orientation of the nitrogen lone pairs on  $P_2pz$  may not be an issue. The key to forming an encapsulated species may, therefore, be finding an appropriate template mechanism to first arrange the ligands around the guest metal of interest before the capping metal is added. We are currently working toward this goal.

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**Supporting Information Available:** Complete X-ray crystallographic data for **1–4** (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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