Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 513–518 **513**
DOI: 10.1021/ic901562d

Mono and Tetranuclear Gold(I) Complexes of Tris(1-benzylimidazole-2-yl)-phosphine

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Received August 5, 2009

The reaction of tris(1-benzylimidazole-2-yl)phosphine, $(Bzim)_3P$, **1**, with $Ph_3AsAuCl$ in 1:1 stoichiometric ratio produced $(Bzim)_3PAuCl$, **2**. The reaction of $(Bzim)_3PAuCl$ with $NaAuCl_4$ in 1:1 stoichiometry in dichloromethane gives an orange-yellow crystalline tetranuclear gold(I) cluster $[\{\mu\text{-}N,N'\text{-}(Bzim)_3PAuCl\}_2Au_2][AuCl_2][AuCl_4]$, **3**. Complex **4**, $[\{\mu\text{-}N,N'\text{-}(Bzim)_3PAuCl\}_2Au_2][AuCl_2]_2$ is formed when the reaction stoichiometry of $(Bzim)_3PAuCl$ and $AuCl_4^-$ is 2:1. The crystal structure of **3** shows the formation of a 12-membered macrocycle with Au···Au distances of ~3.0 Å. The structures of $(Bzim)_3PAuCl$ and **3** show Au···H−C interactions ranging from 2.57 to 2.95 Å. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$), $a = 9.1927(5)$, $b = 13.528(2)$, $c = 22.995(2)$ Å, and $\beta = 94.537(5)°$. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$), $a = 13.785(4)$, $b = 21.426(6)$, $c = 25.203(8)$ Å, and $\beta = 96.51(6)°$.

Introduction

Weak gold−gold, aurophilic attractive interactions[1] arise from correlation effects strongly enhanced by relativistic contributions.[1] Aurophilic attractions are weaker than covalent or ionic bonds but stronger than van der Waals contacts and comparable to hydrogen bonds.[1a,c] In the case of mononuclear Au(I) complexes, the Au···Au contacts are 3.00−3.50 Å and associated with a bond energy in the order of 21−46 kJ mol^{-1} as calculated by theoretical and experimental methods.[2] Au(I) complexes of the type L−Au−X with L = phosphine ligands in particular and X = halide or pseudohalide are able to aggregate into pairs, rings, and chains.[3] In the monomeric complexes the Au(I) coordination geometry is very close to linear while the presence of gold−gold interaction produces a deviation in which the gold atoms are drawn together slightly.

Since aurophilic bonding is directional,[4] the energetic and structural similarities between aurophilic and hydrogen bonding suggested the use of aurophilic attraction to control the supramolecular frameworks of Au(I) complexes. Several studies demonstrated that aurophilic interaction could be used to build supramolecular architectures equivalent to those created by hydrogen bonding.[5] Exploring aurophilicity in the formation of supramolecular structures and secondary interactions in the solid state has received considerable interest. Also non conventional hydrogen bonding such as C−H···Cl[6] or π−π interactions[7] have been found to exist along with the Au···Au interaction in crystal packing.

Gold(I) is an electron rich, soft metal ion and forms stable compounds with soft element ligands. Thus most gold(I) chemistry has sulfur, phosphorus, or carbon containing ligands.[8] However, Au(I) also shows moderate affinity toward nitrogen ligands although the structure of $[Au(NH_3)_2]Br$

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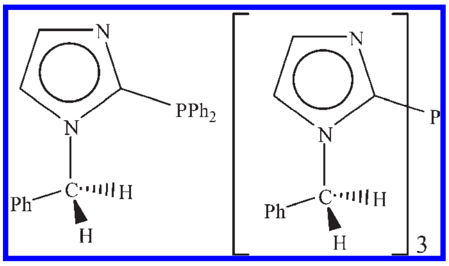
Chart 1. Structure of (1-Benzylimidazole-2-yl)phosphine, (Bzim)Ph_2P, and Tris(1-benzylimidazole-2-yl)phosphine, $(Bzim)_3P$



was reported about sixty years[9] later than that of the analogous silver complex.[10] Several Au(I)−N complexes have been described with amines,[11] ketimines,[12] nitriles,[13] pyrazolates,[14] poly(pyrazolyl)borates,[15] amidinates,[16] benzylimidazolates, and carbeniates.[17] A pentacoordinate nitrido Au(I) cluster$[\mu_5\text{-N}(AuPPh_3)_5]^{2+}$ has been structurally characterized.[18]

In this study we present the coordination chemistry of the P,N-donor ligand tris(1-benzylimidazole-2-yl)phosphine, $(Bzim)_3P$, (Chart 1), with Au(I). The new tertiary phosphine ligand is similar to poly(pyrazol-1-yl)borates.[19] Previous investigations with the (1-benzylimidazole-2-yl)phosphine analogue, (Bzim)Ph_2P, demonstrated that it can react at the P atom forming complexes such as (Bzim)Ph_2PAuCl[20] and [(Bzim)Ph_2PMCl(cod)] (M = Rh(I), Ir(I)),[21] or at P and N centers, as a bidentate ligand, forming dinuclear cationic complexes such as $[\mu\text{-(Bzim)}Ph_2PM]_2[X]_2$ (M = Au(I), Ag(I); X = PF_6^-, BF_4^-, NO_3^-),[22] $[\mu\text{-(Bzim)}Ph_2PHgClO_4]_2[ClO_4]_2$,[23] and $[\{\mu\text{-(Bzim)}Ph_2PM(cod)\}_2][BF_4]_2$ (M = Rh(I), Ir(I)),[21] or $[(\mu\text{-(Bzim)}Ph_2P)_3M_2][X]_2$ (M = Ag(I), Cu(I); X = $CF_3SO_3^-$, BF_4^-).[24] C−H bond activation of one of the phenyl rings of the (Bzim)Ph_2P ligand was observed by adding $[\{Ir(\mu\text{-Cl})(cod)\}_2]$ to [(Bzim)Ph_2PIrCl(cod)] to give the hydride complex $[IrCl(cod)\{\mu\text{-PPh}(C_6H_4)\text{-BzIm}\}IrHCl(cod)]$.[25] Here we report the X-ray crystal structures of $(Bzim)_3PAuCl$, **2**, and $[\mu\text{-}N,N'\text{-}\{(Bzim)_3PAuCl\}_2Au_2][AuCl_2][AuCl_4]$, **3**, which show that $(Bzim)_3P$ ligand is unexpectedly capable of giving rise to secondary interactions involving Au and H.

Experimental Section

Synthesis of $[\{(Bzim)Ph_2PAuCl\}_2AuCl_2]Cl$ and$[\{(Bzim)Ph_2PAuCl\}_2AuCl_2]BF_4$. To a solution of (Bzim)Ph_2PAuCl[20] (0.066 g; 0.155 mmol) in 6 mL of degassed CH_2Cl_2 was added solid $NaAuCl_4\cdot 2H_2O$ (0.023 g; 0.0575 mmol), and the reaction mixture was stirred overnight. The colorless solution slowly turns to yellow, and the formation of a white precipitate of NaCl was observed. The solution was then filtered and pumped down to dryness. The crude compound was washed with hexane and crystallized by CH_2Cl_2 and hexane. Yield 75%. *Anal.* Calcd for $C_{44}H_{38}N_4Au_3Cl_5P_2$: C, 36.37; H, 2.64; N, 3.86. Found: C, 36.49; H, 2.84; N, 3.64. ^1H NMR ($CDCl_3$, δ, 295 K): 4.83 (s), 5.08 (s), 5.39 (s), 5.59 (s), 5.64, (s), 6.70−6.75 (m), 6.96−7.00 (m), 7.09−7.98 (m). ^{31}P NMR ($CDCl_3$, δ, 295 K): 12.47 (s), 15.46 (s), 19.13 (s), 23.44 (s). IR (C−H stretching region, cm^{-1}): 3117.8, 3054.7, 3033.2, 2957.9, 2925.7, 2856.1. After treatment of $[\{(Bzim)Ph_2PAuCl\}_2AuCl_2]Cl$ with a stoichiometric amount of $AgBF_4$, the complex $[\{(Bzim)Ph_2PAuCl\}_2AuCl_2]BF_4$ was formed in a quantitative yield. The elimination of the chloride counterion resulted in a stable complex in solution as highlighted by its NMR. *Anal.* Calcd for $C_{44}H_{38}N_4Au_3Cl_4P_2BF_4$: C, 35.13; H, 2.55; N, 3.72. Found: C, 35.41; H, 2.72; N, 3.60. ^1H NMR ($CDCl_3$, δ, 295 K): 4.78 (s, 2H), 4.90 (s, 2H), 6.71−6.75 (m, 4H) 7.13−8.02 (m, 26H), 8.42 (s, 4H). ^{31}P NMR ($CDCl_3$, δ, 295 K): 23.38 (s).

Synthesis of $(Bzim)_3P$, 1. The synthesis can be carried out in two alternative ways as reported in literature. Both methods are successful and give similar yields.[26] The following is a slightly modified synthesis of the one reported for $(py)_3P$ by Schmidbaur. To a stirred anhydrous diethyl ether solution (15 mL) of 1-benzylimidazole (0.4514 g, 2.85×10^{-3} mol) cooled to −70 °C, under a nitrogen atmosphere, was added a 2.5 M hexane solution of BuLi (1.14 mL, 2.85×10^{-3} mol). After 2 h the temperature of the yellow solution was raised to −30 °C for 30 min then cooled again to − 90 °C. At this point 2 mL of a diethyl ether solution containing PCl_3 (0.083 mL, 0.95×10^{-3} mol) was added dropwise over 1 h. After 2 h the mixture was left to reach room temperature, and stirred overnight. The white suspension obtained was extracted with 11 mL of 2 M H_2SO_4, and then the aqueous phase was neutralized by a saturated solution of $NaHCO_3$. The white waxy solid which formed was extracted with dichloromethane. The yellow solution was dried over anhydrous Na_2SO_4 and evaporated to dryness. A 0.319 g portion of an oily yellow solid was obtained (yield ~66%). The $(BzIm)_3P$ ligand is easily oxidized, so no satisfactory analysis was obtained. $(BzIm)_3P$ *must* be kept under a nitrogen atmosphere. ^{31}P $\{^1H\}$NMR (acetone-d^6; δ, 295 K): −61.76 (s). A signal at 1.75 (s) is also present. This signal is less than 10% of the ligand signal at −61.76 ppm, and it can be assigned to the phosphine oxide.^1H NMR (acetone-d^6; δ, 295 K): 5.25 (s, 6H), 7.03−7.42 (m, 21H). IR (aromatic and aliphatic C−H stretching region, cm^{-1}): 3103, 3090 (shoulder), 3062.8, 3030, 3005.4, 2929.4.

Synthesis of $(BzIm)_3PAuCl$, 2. $(BzIm)_3P$, 0.159 g (3.15×10^{-4} mol), under a nitrogen atmosphere, was dissolved in 5.5 mL

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of CH_2Cl_2 and cooled to 0 °C. To this pale yellow solution was added solid $Ph_3AsAuCl$ (0.1698 g, 3.15×10^{-4} mol). The clear solution was stirred for about 1 h. The completeness of the reaction was followed by TLC (formation of free Ph_3As). The solution was then evaporated off under reduced pressure to dryness, leaving a yellow oil. The product was treated several times with hexane until a solid was obtained which dissolved in a few milliliters of CH_2Cl_2. The solution was layered with hexane to form colorless crystals suitable for an X-ray structure determination (0.101 g; yield 43%). Mp 216−219 °C.

Anal. Calcd for $C_{30}H_{27}N_6PAuCl$: C, 49.03; N, 11.43; H, 3.70. Found: C, 48.92; N, 11.43; H, 3.86. $^{31}P\{^1H\}$NMR (acetone-d^6; δ, 295 K): 19.75 (broad). ^1H NMR (acetone-d^6; δ, 295 K): 5.43 (s, 6H), 7.07−7.1 (m, 6H), 7.19−7.2 (t, 3H), 7.23−7.28 (m, 9H), 7.37−7.38 (t, 3H). IR (aromatic and aliphatic C−H stretching region, cm^{-1}): 3114.3, 3094.2, 3063.3, 3034.1, 3008.6, 2069.5, 2931.8.

Synthesis of [{*μ*-*N*,*N′*-(Bzim)$_3$PAuCl}$_2$Au$_2$][AuCl$_2$][AuCl$_4$], 3 and [{*μ*-*N*,*N′*-(Bzim)$_3$PAuCl}$_2$Au$_2$][AuCl$_2$]$_2$, 4. To a stirred CH_2Cl_2 solution (6 mL) of **2** (0.0355 g, 4.72×10^{-5} mol), under a nitrogen atmosphere, was added the salt $NaAuCl_4$ (0.01707 g, 4.72×10^{-5} mol). The mixture was stirred overnight at room temperature. The yellow solution was filtered through Celite and layered with hexane. After few days at −4 °C orange crystals grew. Yield 65% (calculated based on complex **2**). In a similar way but using a 2:1 molar ratio of (Bzim)$_3$PAuCl to $NaAuCl_4$, the white microcrystalline compound **4** was obtained (yield 80%).

Anal. Calcd for **3**, $C_{60}H_{54}N_{12}Cl_8P_2Au_6$: C, 29.17 ; H, 2.20 (2.35); N, 6.80 (6.63). Found: C, 29.03; H, 2.35; N, 6.63. *Anal.* Calcd for **4**, $C_{60}H_{54}N_{12}Cl_6P_2Au_6$: C, 30.03; H, 2.27; N, 7.00. Found: C, 29.75; H, 2.29; N, 7.12. NMR spectra for **3** and **4**. $^{31}P\{^1H\}$NMR (CD_2Cl_2; δ, 293 K) 24.09 (s). ^1H NMR (CD_2Cl_2; δ, 293 K): 4.83 (s, broad, 2H), 5.40 (m, 8H), 5.6 (d, broad, 2H), 6.95−7.20 (m, 10H), 7.23−7.65 (m, 28H), 7.95 (s, 4H). IR (aromatic and aliphatic C−H stretching region, cm^{-1}): 3169, 3139, 3112.8, 3059.5, 3027.2, 2933.8, 2900, 2818, 2782, 2686, 2658.6, 2621.4, 2594.7.

Structure Determination. The X-ray structures of the prismatic crystals of **2** (colorless) and **3** (orange-yellow) were solved in the monoclinic space groups $P2_1/n$ and $P2_1/c$, respectively. The unit-cell dimensions were determined by least-squares refinement of the setting angles of 24 high angle reflections carefully centered. X-ray diffraction effects were collected on a Rigaku AFC5R diffractometer using graphite monochromated Cu Kα radiation and a 12 kV rotating anode generator. Intensity data were collected by $\omega/2\theta$-technique to a maximum 2θ value of about 124°, **2**, and 121°, **3**. Three standard reflections were measured every 100 reflections which were found to remain constant. Corrections for Lorentz and polarization were applied together with an empirical absorption correction that uses scan data of three reflections at angles of about 90°. The minimum normalized factors were in the range 0.55. Only the independent reflections, which met the condition $I > 3\sigma(I)$, were used in the subsequent calculations.

Structures **2** and **3** were solved by Patterson and subsequent Fourier syntheses and refined by full-matrix least-squares method with the minimized function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)^2$. The hydrogen atoms were included at calculated positions and not refined. All the non-hydrogen atoms were refined anisotropically while for complex **3** only the Au, Cl, and P atoms were refined anisotropically. All the hydrogen atoms were given the isotropic thermal factors of the parent carbon atoms and not refined. The refinement converged at R1 = 0.048 and wR2 = 0.060, **2**, and R1 = 0.068 and wR2 = 0.087, **3**. All calculations were performed using the TEXAN crystallographic software package[27] and the SIR CAOS structure determination package.[28] Scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography.[29]

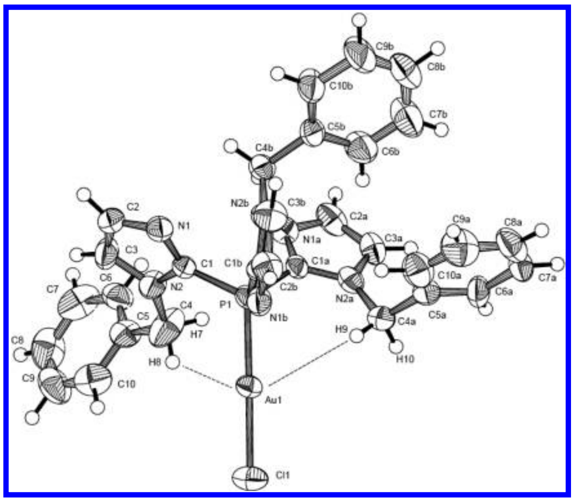

Figure 1. Thermal ellipsoid plot of (Bzim)$_3$PAuCl, **2**. Ellipsoids are shown at 40% probability.

Results and Discussion

The reaction of (Bzim)$_3$P, **1**, with $Ph_3AsAuCl$ in 1:1 stoichiometric ratio formed (Bzim)$_3$PAuCl, **2**, by displacement of the Ph_3As ligand. The crystal structure of **2** is shown in Figure 1. Crystal data and selected bond lengths and angles are listed in Tables 1 and 2. The structure of **2** consists of monomeric units with Au(I) atoms in a nearly linear arrangement with a P−Au−Cl angle of 176.65(8)°. The P−Au−Cl angle of 176.65(8)° in **2** is close to the value of 175.1(3)° reported for the analogous complex (Bzim)Ph$_2$PAuCl[20] in which intermolecular Au···Au contacts of 3.03(2) Å are present. The absence of Au···Au interactions in **2** is not reflected in the P−Au−Cl angle, which is not as close to linear as in R$_3$PAuCl complexes such as Et$_3$PAuCl, Pr$_3$PAuCl, Ph$_3$PAuCl, and (furil)$_3$PAuCl (178.0°−178.9°). The Au−P bond length of 2.216(2) Å found in **2** is shorter than in (Bzim)Ph$_2$PAuCl, 2.239(3) Å.[20] Few examples of such short Au−P bond length have been reported: Cl$_3$PAuCl, 2.198(2) Å;[30] Me$_3$PAuOSiMe$_3$, 2.210(2) Å;[31] (furyl)$_3$PAuCl, 2.209(3) Å.[32]

The crystal structure of (Bzim)$_3$PAuCl is characterized by an interesting feature not seen in Au(I) complexes of benzylimidazolylphosphane. In (Bzim)Ph$_2$PAuCl, the methylene hydrogen atoms of the benzyl groups are placed close to the gold atoms by rotation of the imidazolyl groups. One benzylimidazolyl group assumes a conformation favorable for the CH$_2$ group to have one hydrogen atom at a close distance from the Au center (Au···H−C 2.62 Å). In spite of the Au···H−C contact and the bulkiness of the 1-benzyl-2-imidazolyl diphenylphosphane, the gold atom is still available to strongly interact with another gold atom at 3.03 Å. In (Bzim)$_3$PAuCl, two benzylimidazolyl groups can position

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Table 1. Crystal Data for Complexes **2** and **3**

	2	**3**
empirical formula	$C_{30}H_{27}AuClN_6P$	$C_{60}H_{54}Au_6Cl_8N_{12}P_2$
formula weight	734.98	2470.57
crystal dimensions (mm)	0.10 × 0.25 × 0.40	0.07 × 0.07 × 0.50
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a (Å)	9.1927(5)	13.785(4)
b (Å)	13.528(2)	21.426(6)
c (Å)	22.995(2)	25.203(8)
β (deg)	94.537(5)	96.51(6)
V (Å^3)	2850.5(6)	7396(1)
Z	4	4
D_c (g/cm^3)	1.712	2.219
reflections collected	5054	8345
independent reflections	4728 (R_{int} = 0.055)	7639 (R_{int} = 0.027)
R1, wR2	0.048, 0.060	0.068, 0.087

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **2** and **3**

	Complex **2**		
Au(1)−Cl(1)	2.276(2)	Au(1)−P(1)	2.216(2)
Cl(1)−Au(1)−P(1)	176.65(8)		
	Complex **3**		
Au(1)−Au(4)	2.989(2)	Au(1)−Au(2)	3.257(3)
Au(1)−Au(3)	3.862(2)	Au(4)−Au(2)	3.962(2)
Au(4)−Au(3)	3.766(2)	Au(2)−Au(3)	3.014(2)
Au(1)−P(1)	2.22(1)	Au(1)−Cl(1)	2.29(1)
Au(4)−N(3)	2.04(3)	Au(2)−P(2)	2.22(1)
Au(2)−Cl(2)	2.27(1)	Au(3)−N(1)	1.98(3)
Au(5)−Cl(4)	2.26(2)	Au(5)−Cl(3)	2.28(3)
Au(6)−Cl(6)	2.63(6)	Au(6)−Cl(7)	2.54(6)
Cl(1)−Au(1)−P(1)	173.5(4)	N(7)−Au(4)−N(3)	173(1)
Cl(2)−Au(2)−P(2)	173.9(4)	N(9)−Au(3)−N(1)	175(1)
Cl(3)−Au(5)−Cl(6)	90(1)	Cl(4)−Au(5)−Cl(6)	88(1)
Cl(4)−Au(5)−Cl(3)	177(1)	Cl(5)−Au(5)−Cl(6)	178(1)
Cl(7)−Au(6)−Cl(8)	163(1)		

one hydrogen atom of each CH_2 group at close distance from gold (2.83 and 2.95 Å) (Figure 2). In a theoretical study on the stability of Au(I) phosphine complexes of the form $[Au(PH_3)_n]^+$ (n = 1−4) and $[Au(PH_3)_nCl]$ (n = 1−3), structures with conformations that allow Au···H (2.691−2.980 Å) were found possible but with a high energy, ~35 kJ mol^{-1}, above the global minimum.[33]

In the crystal packing of $(Bzim)_3PAuCl$, **2**, the molecules are connected by two kinds of weak interactions to form a net: $\pi-\pi$ interactions and C−H···Cl hydrogen bonds. The net is formed by chains along the b axis with lateral connections along the c axis. Along the chains the molecules are connected by two weak $\pi-\pi$ interactions between the centroids of the imidazolyl and the benzyl rings and by two C−H···Cl hydrogen bonds (Table 3, first four entries). The chains are in turn connected by other very long C−H···Cl hydrogen bonds (Table 3, entries 5−7).

In the attempt to obtain a mixed Au(I)/Au(III) complex, the reaction of **2** with $NaAuCl_4$ in a 1:1 stoichiometry was perfomed. From the reaction mixture, the tetranuclear complex **3** was isolated as an orange-yellow crystalline compound (Scheme 1). The presence of the $AuCl_4^-$ in **3** as the counterion is indicative of an excess of the Au(III) salt in the reaction mixture. In fact, when the reaction molar ratio of **2** with $NaAuCl_4$ is 2:1, the yield is higher, about 80%, and only $AuCl_2^-$ as a counterion is present, complex **4**.

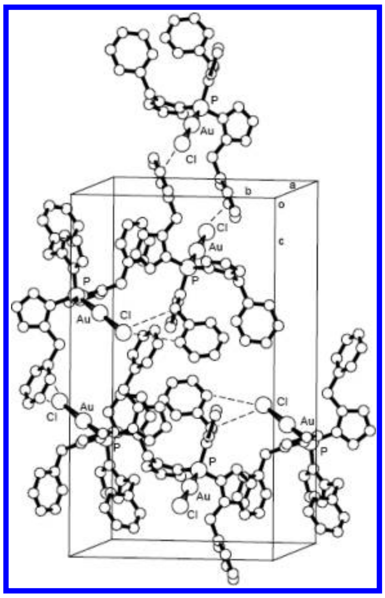

Figure 2. Crystal packing of complex $(Bzim)_3PAuCl$, **2**, showing the secondary interactions.

The reduction of the $AuCl_4^-$ ion is well-established when phosphorus or sulfur ligands are used as reducing agents.[34] Also the reduction of Au(III) haloammine complexes by iodide has been described.[35] The reaction of Na[3,5-Ph_2pz] with Au(III)pyCl_3 in tetrahydrofuran (THF) produced the mixed valence Au(I)/Au(III) complex $[Au_3(3,5\text{-}Ph_2pz)_3Cl_2]$.[36] It is likely that compounds **3** and **4** result from the reduction of $AuCl_4^-$ with formation of the oxidized phosphine after coordination of the Au(III) to the nitrogen atoms of the imidazole rings of the $(Bzim)_3PAuCl$. When (Bzim)Ph_2PAuCl was reacted[37] with $AuCl_4^-$, the mixed valence complex $[\{(Bzim)Ph_2PAuCl\}_2AuCl_2]Cl$ was isolated where the Au(III) center is coordinated to two nitrogen atoms from two (Bzim)Ph_2PAuCl units.[37]

Crystal data, selected bond lengths and angles for complex **3** are listed in Tables 1 and 3. Complex **3** (Figure 3) crystallizes in the monoclinic space group $P2_1/c$ (Z = 4). It consists of a 12-membered macrocycle containing two of the four gold atoms coordinated to two $(Bzim)_3P$ ligands. The mean Au−N distance is 2.01 Å. It is in the range of the bond lengths found in related tetranuclear nitrogen clusters complexes such as $[\mu\text{-}3,5\text{-}{}^tBu_2pzAu]_4$,[38] $[(dppm)_2Au_4(3,5\text{-}Ph_2\text{-}Pz)_2][NO_3]_2$,[39] $[Au_4(ArNC(H)NAr)_4]$,[16] and $[Au_4(\mu_3\text{-}L)(PPh_3)_4][BF_4]_2$, L = 8-aminoquinoline.[40] The other two gold atoms are coordinated to the phosphorus atom of $(Bzim)_3P$ ligand with both P−Au bond lengths of 2.22(1) Å. They complete their bicoordination with two chloride atoms with Au−Cl = ~2.28 Å. The strong deviation from linearity of the

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Table 3. Distances (Å) between Centroids of Imidazolyl and Benzyl Rings and C−H···Cl Hydrogen Bond Distances in the Crystal Packing of **2**

		dist. (Å)
C(1)−C(3) imidazolyl (*x*,*y*,*z*)	C(5A)-C(10A) benzyl (1/2−*x*,1/2+*y*,1/2−*z*)	3.96
C(5A)−C(10A) benzyl (*x*,*y*,*z*)	C(1)−C(3) imidazolyl [(1/2−*x*,−1/2+*y*,1/2−*z*) + (2,−1,0)]	3.94
Cl (*x*,*y*,*z*)	H−C(4B) [(1/2−*x*,1/2+*y*,1/2−*z*) + (2,−1,0)]	2.78
	H−C(10B) [(1/2−*x*,1/2+*y*,1/2−*z*) + (2,−1,0)]	2.90
	H−C(7) [(−*x*,−*y*,−*z*) + (1,0,0)]	2.89
	H−C(9) [(−*x*,−*y*,−*z*) + (2,1,0)]	3.00
	H−C(10) [(−*x*,−*y*,−*z*) + (2,1,0)]	3.14

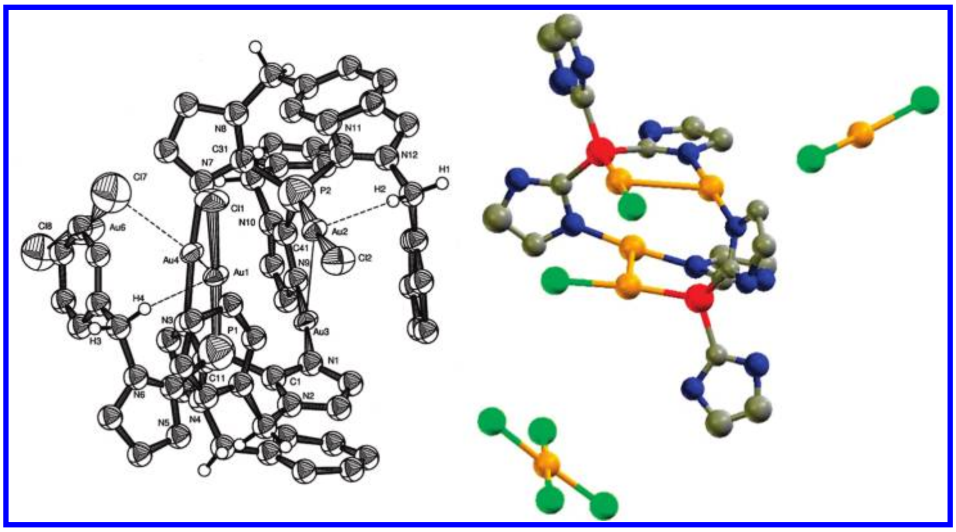
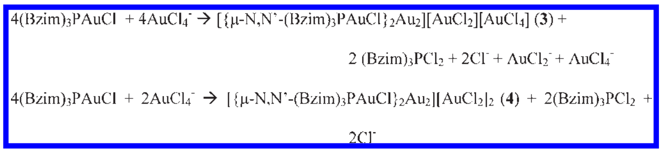


Figure 3. Structural plots of [{*μ*-*N*,*N*′-(Bzim)3PAuCl}2Au2][AuCl2][AuCl4], **3**. Au(1)···Au(4) = 2.989(2), Au(2)···Au(3) = 3.014(2), Au(1)···Au(2) = 3.257(3), Au(3)···Au(4) = 3.766(2), Au(2)···H(2) = 2.48, Au(1)···H(4) = 2.67, and Au(4)−Cl(7) = 3.33(5) Å.

angles: N(1)−Au(3)−N(9) 175(1)°, N(3)−Au(4)−N(7) 173(1)°, P(1)−Au(1)−Cl(1) 173.5(4)°, and P(2)−Au(2)−Cl(2) 173.9(4)° is consistent with the aurophilic interactions Au(2)···Au(3) 3.014(2) and Au(1)···Au(4) 2.989(2) Å. The tetranuclear arrangement is composed of two dinuclear moieties that rotate around each other by approximately 77° (Figure 3) and interact through Au(1)···Au(2) 3.257(3) and Au(3)···Au(4) 3.766(2) Å). The latter distance is on the long edge of the range considered for gold−gold interactions, 2.8−3.6 Å, and it may originate from Coulombic repulsions between two formally positive Au(I) centers even though short distances between Au(I) atoms supporting the same charge (+ + or − −) have been found.[41]

In complex **3** each methylene group has one hydrogen atom that interacts with a gold center: H(4)···Au(1) = 2.59 Å, Au(1)···H(4)−C(24) = 130°, H(2)···Au(2) = 2.57 Å, and Au(2)···H(2)−C(54) = 139°. The nature of hydrogen−metal interactions has been extensively debated; they can involve transition metal atoms as hydrogen bond donors or acceptors.[42]

Scheme 1



$$4(\mathrm{Bzim})_3\mathrm{PAuCl} + 4\mathrm{AuCl_4}^- \rightarrow [\{\mu\text{-N,N'-}(\mathrm{Bzim})_3\mathrm{PAuCl}\}_2\mathrm{Au_2}][\mathrm{AuCl_2}][\mathrm{AuCl_4}]\ (\mathbf{3}) + 2\,(\mathrm{Bzim})_3\mathrm{PCl_2} + 2\mathrm{Cl}^- + \mathrm{AuCl_2}^- + \mathrm{AuCl_4}^-$$

$$4(\mathrm{Bzim})_3\mathrm{PAuCl} + 2\mathrm{AuCl_4}^- \rightarrow [\{\mu\text{-N,N'-}(\mathrm{Bzim})_3\mathrm{PAuCl}\}_2\mathrm{Au_2}][\mathrm{AuCl_2}]_2\ (\mathbf{4}) + 2(\mathrm{Bzim})_3\mathrm{PCl_2} + 2\mathrm{Cl}^-$$

Baukova et al.[43] described the formation of Au···H−C interactions in diphenylmethane and diphenylethane organogold derivatives and classified them as agostic interactions on the basis of the infrared spectroscopic evidence for the shift of about 100 cm^{-1} to lower frequency of the C−H stretches. On the basis of the Brookhart study,[42] the intramolecular hydrogen−gold interactions present in complex **2** are compatible with an electrostatic interaction, analogous to the closed shell C−H···Co interaction in $[Et_3NH][Co(CO)_4]$. Lippard[42e] has used the term anagostic for such interactions. The ligand $(Bzim)_3P$ shows a peak at 2929 cm^{-1} in the infrared that can be assigned to the C−H stretch of the methylene in the benzyl group. When the ligand is coordinated to the gold atom in $(Bzim)_3PAuCl$, **2**, a new peak at 2969 cm^{-1} appears. The position of this signal is not compatible with an agostic Au···H−C interaction but may represent an anagostic interaction. The crystallographic data, however, is well matched for an agostic interaction wherein the M−H bond length is in the range of 2.3−2.9 Å and a M−H−C bond angle is 110−170°.[42] Packing forces positioning the methylene groups close to the gold atoms may be involved. The IR spectrum of the tetranuclear gold(I) complex, **3**, in the region 4000−2400 cm^{-1} is

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more complicated than that recorded for the mononuclear compound. The signals of the C−H stretch of the aromatic protons are shifted at higher energy with respect to the free ligand. The aliphatic C−H bonds show several signals below the 3000 cm^{-1} region. A large indented band from 2820 cm^{-1} to 2590 cm^{-1} was observed while the new band at 2900 cm^{-1} could be due to an anagostic Au···H−C interaction.

The ^{1}H NMR spectrum of compound **3** shows three groups of signals for the CH_2 benzyl group, 2H at higher field, 2H at lower field when compared with the CH_2 benzyl of the $(Bzim)_3PAuCl$, and 8H due to the four imidazoles involved in the N−Au−N bonds. The diastereoscopic nature of the CH_2 benzyl groups complicate further analysis relative to any Au···H−C interactions.

The interest in tetranuclear gold clusters is due to their potential application as precursors for CO and olefin oxidation,[44] their structural features and the presence of short Au···Au interactions possibly influencing the optoelectronic properties observed in various polynuclear Au(I) compounds.[45]

Acknowledgment. This work was supported by grants from University of Camerino and CNR (Roma) and The Robert A. Welch Foundation, Houston, Texas.

Supporting Information Available: The .cif files, the IR spectra for the aromatic and the aliphatic C−H stretches, an the ^{1}H NMR of complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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