Structural, photoluminescence, and theoretical DFT studies of gold(I) and silver(I) metallacycle dinuclear complexes of 1-methylbenzimidazolidiphenyl phosphine (MBDP) ligand.

Darkus E. Jenkins¹, Zerihun Assefa^{2*}

Abstract

The synthesis and structural characterization of the bridging ligand, 1-methyl benzimidazole diphenylphosphine (MBDP) and its coordination with Au(I) and Ag(I) metal ions is reported. Two ligands coordinate to the metal ions in head to tail fashion forming a metallacycle coordination consisting of strong M-M bonding interaction with Au-Au = 2.808 and Ag – Ag = 3.017 Å. Linear coordination is observed for the gold, while the silver shows distorted tetrahedral arrangement. X-ray crystal data of [(MBDP)₂Au₂](CH₃CN)(BF₄)₂ (**2**) crystallizes in the monoclinic system with the space group of *P*2₁/*n* with cell constants of *a* = 8.9993 (8) Å, *b* = 19.6166 (18) Å, *c* = 13.4484 (12) Å, β = 100.966 (2)°, *R* = 0.026, and *R_w* = 0.064. The structure of [(MBDP)₂(CH₃CN)₄Ag₂](BF₄)₂, (**3**) crystallizes in the *P*(-)*1* space group and the unit cell is *a* = 10.5423(10) Å, *b* = 10.7638(10) Å, *c* = 12.3530(12) Å; α = 88.592(3)°, β = 73.097(3)°, γ = 84.422(3)°, *V* = 1334.8 (2) Å³ with *Z* = 1, *R* = 0.034 and *R_w* = 0.093. The coordinating ligand as well as both dinuclear compounds reported here are luminescent in the near UV region. As supported by the DFT theoretical work, the emission is suggested to be primarily ligand based π - π^* transition.

Keywords: benzimidazole, Au(I) dimer, Ag(I) dimer, phosphine

1. Introduction.

Phosphine ligands are well known for their ability to coordinate to group 11 metal ions particularly to Au(I) and Ag(I) centers [1-8]. Due to their steric effects and π -acceptor abilities, tertiary phosphines are one of the most studied groups of ligands for gold (I) complexes [1-8]. Bis(diphenylphosphino)methane (dppm) and bis(dicyclohexylphosphino)methane (dcpm) are representative of the diphosphine ligands. The dppm, dcpm and related ligands are very flexible and capable of bringing two gold atoms as close as 2.4 - 3.6 Å [9-11] with varying geometries including open and metallacycle features with Au-Au separations of 2.8 - 3.1 Å [12-14].

Over the past four decades attention has been given to bifunctional ligands with regards to bringing two metal atoms in close proximity [15-18]. Several types of ligands have attracted attention including the N-, P-type ligands. Diphenylphosphinopyridine (dppy), dimethylphosphinopyridine (dmpp), and 2-(diphenylphosphino)-1-benzylimidazole (BzImPh₂P) are representative of the mixed-donor species commonly used to prepare Au(I) dimers[12-14, 19- 20]. These ligands follow the Lewis soft acid/base chemistry when coordinating with group 11 metals. Although N is a lesser soft base than P, its ability to bind with Au(I) is well documented [21-25] including the work conducted by Fackler et al. on amidinate ligands [26-27]. The ability to bring two Au(I) atoms in close proximity is a goal for many research groups because of the fascinating photoluminescence these types of compounds reveal. Hence, the bridging N, P ligands not only coordinate as monodentate ligand, they also have the ability to act as bidentate ligands through the two donor atoms and bring homo- and hetero-nuclear atoms together with short distances.

Burini and co-workers have extensively studied the N, P type ligand of (1-benzyl-2-imidazolyl) diphenyl-phosphine (BzimPh₂P) to understand the behavior of coordination with various metal systems [15-18]. They were able to utilize the monodentate and bidentate feature of the BzimPh₂P by examining complexes with Au(I), Ag(I), Cu(I), Rh(I), Ir(I), Hg(II), Zn(II), and Cd(II) metal ions. In the Au (I) structure, the coordination is found to be monodentate with a near linear geometry of the P-Au-Cl bond angle with the ligand unassisted intermolecular Au – Au distance of 3.306 Å.

Bachechi along with Burini and co-workers also studied the X-ray crystal structure of silver complexes with the same ligand [18] and interesting geometries around the metal ions were observed. The ligand is thought to offer stability for metal – metal interactions including the lighter group 11 metals that possess the same abilities to coordinate two or more metal atoms in close proximity to each other. Rigid ligands such as dmpp are found to constrain the metal-metal separation, and [dmpp₂Au₂](BF₄)₂ was found to have an Au -Au separation of only 2.776 Å [28]. More recently, Ag(I) complexes of similar ligands have been shown to exhibit argentophilic bonding analogous to the Au(I) systems [29]. A number of other interesting structures consisting of Cu(I) and Ag(I) metal ions with N, P ligands have been characterized [15-18, 30-33]. These compounds also have interesting luminescent properties, hence further supporting the desire for using this type of ligand.

In this manuscript we report the coordination of the methyl benzimidazolidiphenyl phosphine (MBDP) ligand to a Au(I) center and compare the structural feature with that of Ag(I) complexes. The structural analysis and luminescence studies are compared for the two types of complexes as well as results from theoretical DFT calculations reported.

2. Experimental

2.1 Materials and methods

Methylbenzimidazole, n-butyllithium (nBuLi), and chlorodiphenylphosphine (PPh₂Cl) were commercially available from the Sigma-Aldrich and used without further purification. The (tht)Au(I) chloride (tht = tetrahydrothiophene) was prepared and purified following the methods of Uson and coworkers [34]. All of the solvents used including tetrahydrofuran (THF), acetonitrile (CH₃CN), dichloromethane (DCM), diethyl ether (Et₂O), chloroform (CHCl₃), and hexanes were degassed using a N₂ purge.

2.2. Physical measurements.

The infrared (IR) spectra were collected using potassium bromide (KBr) pellets on a Shimadzu IRPrestige21 Fourier-Transform infrared spectrophotometer, over the range 4000-400 cm⁻¹. Spectra were collected at 64 scans and a resolution of 1cm⁻¹. The ultraviolet and visible (UV-Vis) spectra were collected using a Shimadzu UV-2401PC UV-Vis spectrometer. The photoluminescence (PL) data were collected using a Photon Technology International (PTI) spectrometer model QM-7/SE, equipped with a Hamamatsu R928P photomultiplier tube with corning filters. Excitation and emission spectra obtained at room temperature and at 77K with liquid nitrogen filled in the cold-finger dewar flask. The instrument operation, data collection, and handling were all controlled using the advanced Felix32 software. Selection of excitation and emission wavelengths are conducted by means of computer controlled autocalibrated “QuadraScopic” monochromators that are equipped with aberration corrected emission and excitation optics.

The proton (¹H) and phosphorus (³¹P) nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz Varian NMR 300 – 411149 FT-NMR spectrometer. Chemical shifts (δ

ppm) were reported relative to an internal standard, tetramethylsilane (TMS) for ^1H , while 85% phosphoric acid (H_3PO_4) was used as an external standard for the ^{31}P NMR in CDCl_3

2.3. Synthesis of 1-methylbenzimidazole diphenylphosphine (MBDP).

The MBDP ligand was synthesized following a modified procedure of the previously reported scheme [35, 37]. In a 250 mL Schlenk flask containing 100 mL THF was added a 6.6085 g (50 mmol) of 1-methylbenzimidazole. The solution was stirred until the solid has dissolved and cooled to $-78\text{ }^\circ\text{C}$ in acetone/dry ice bath. To this solution 31.25 mL (50 mmol) of n-BuLi was added slowly while stirring for 1 hour. Then 9 mL (50 mmol) of chlorodiphenylphosphine was added drop-wise. The solution was allowed to warm to room temperature and stirred for 3 hours. The solvent was then evacuated by vacuum suction to yield an orange foamy product. To this solution Et_2O and then H_2O (50 mL each) was added and the organic layer collected. The Et_2O was removed under vacuum to produce an oily product. The product was sonicated for 10 minutes in warm hexanes. A cloudy layer was then formed, collected, and allowed to cool. X-ray quality crystals were produced. $^{31}\text{P}\{^1\text{H}\}$ NMR -25.6 ppm with phosphoric acid standard.

2.4. Preparation of (MBDP)Au(I) chloride (I)

To a 25 mL round-bottom flask a 0.064 g (0.20 mmol) (tht)AuCl was dissolved in 10 mL THF. To this solution a 0.064 g (0.20 mmol) of the ligand was added and allowed to stir for 3 hours. The solution was concentrated under high pressure vacuum to approximately 3 mL then layered with Et_2O . The flask was placed in the freezer overnight and x-ray quality crystals were formed. ^1H NMR in CDCl_3 (ppm); 3.98 (s, 1H), 7.33 – 7.54 (m, 5H), 7.58 – 7.60 (m, 6H), and

7.70 – 7.83 (m, 5H). The $^{31}\text{P}\{^1\text{H}\}$ NMR 14.59 (s).

2.5 Preparation of $[(\text{MBDP})_2\text{Au}_2](\text{CH}_3\text{CN})(\text{BF}_4)_2$ (**2**)

In a 25 mL round-bottom flask, a 0.064 g (0.20 mmol) of (tht)AuCl was dissolved in 10 mL CH_3CN . A 0.040 g (0.20 mmol) of AgBF_4 was added to the flask and stirred for 5 minutes. A white precipitate formed, which was filtered through a pad of Celite®. To the filtrate, the ligand MBDP (0.064 g, 0.20 mmol) was added and allowed to stir for 3 hours. The solution was concentrated under vacuum to approximately 3 mL. The solution was then layered with Et_2O and placed in a freezer. X-ray quality crystals were obtained after 4 days.

2.6 Preparation of $[(\text{MBDP})_2\text{Ag}_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (**3**).

The silver(I) tetrafluoroborate complex **3** with the MBDP ligand (1:1 molar ratio) was prepared in a 25 mL round-bottom flask covered with aluminum foil. A 0.0397 g AgBF_4 (0.20 mmol) was dissolved in 10 mL CH_3CN and to this solution MBDP ligand (0.0637 g, 0.20 mmol) was added and allowed to stir for 3 hours. The solution was concentrated under vacuum to approximately 3 mL. The partial removal of the solvent was followed by layering with Et_2O . The flask was then placed in the refrigerator, where X-ray quality crystals were formed after 4 days.

2.7. X-ray Crystallography

X-ray data were collected using a Bruker AXS SMART X2S system based diffractometer equipped with a CCD 485 Breeze detector and a Ricor K535 power supply unit. A suitable crystal was chosen and mounted on a pin using a micro-mount needle from Bruker Corporation using Paratone-N oil purchased from Hampton Research. The diffraction data for the determination of the crystal structures were collected on CD-R using the Bruker CCD 485

Breeze detector for cell refinement, and data reduction with Apex2 and X-SHELL. For structural display, report and visualization the Mercury software version 3.5.1 from CCDC 2001-2014 was used. The structures were solved using the Apex 2 series of software program from Bruker and by direct methods. The XSHELL program(s) was used to refine the structures, while molecular graphics were done using the APEX2 software.

2.8. Computational Details

The Gaussian '09 software package [36] was used for theoretical calculations at the Density Functional Theory (DFT) level. Geometry optimizations and frequency calculations were computed with Becke three-parameter exchange with the Perdew–Wang 1991 correlation (B3PW91). The excitation energies and oscillator strengths were performed using the optimized structures of the ligand and the complexes without any consideration for solvent by time-dependent (TD)-DFT with B3PW91. The predicted absorption spectra of the optimized structures were accomplished by time-dependent density functional theory (TD-DFT) without consideration of any solvent effect. The LANL2DZ effective core potentials and valence basis set were used to describe the valence electrons of gold. Phosphorus, carbon, and hydrogen were described with 6-31+G*, 6-31G*, and 6-31G basis sets, respectively. Molecular isodensity diagrams (Isovalues: 0.02 atomic units) of molecular orbital estimations were created using the GaussView 5 software (Gaussian Inc.).

3. Results and discussion

3.1 Synthesis

The ligand MBDP has been previously synthesized in 1982 by the Whiteside group, and a modified version of the original synthesis route [35, 37] was followed, where the starting reactants were changed to 1-methylbenzimidazole and chloro-diphenylphosphine. Our group was able to grow X-ray quality single crystals and reported the structure for the first time recently [38]. However, no complexation studies or structural work has been reported for this potentially bidentate ligand, although complexes of the related ligand, 2-(diphenylphosphino)-1-methylimidazole have been reported [39]. It was of much interest to understand the effect of the benzene ring on the reactivity and coordination ability of the phosphine-imidazole group. Particular interest for our group has been to understand the ability of the MBDP ligand to allow the facile formation of Au(I) and Ag(I) homo- and heterobimetallic complexes that may possess interesting structural and photophysical properties.

Scheme 1: Synthetic scheme of compound 2

The gold complex was prepared by mixing the starting (tht)AuCl and MBDP ligand in a 1:1 ratio. Direct addition of the ligand to the gold starting material provided the mononuclear

(MBDP)AuCl species which shows coordination through the P atom of the ligand with chloride atom intact in the coordination. Although the metallacycle coordinated compound **2** was also prepared in a 1:1 ratio, removal of the chloride ion by the addition of the AgBF₄ was a necessary first step. Addition of the ligand after filtering off the AgCl precipitate provided compound **2**. Similarly, compound **3** was prepared in 1:1 ratio using the AgBF₄ starting material. Hence in both metal ions, the use of a starting material with a weakly bound and/or labile anion was a necessary condition for the metallacycle coordination.

3.2 Solvent and temperature effect on synthetic procedure and product stability

Synthesis of the products was attempted in several solvent systems including THF/Et₂O, THF/CH₃CN/Et₂O, and CH₃CN. X-ray quality crystals of (MBDP)AuCl, **1** were obtained using the THF/Et₂O (synthesis/crystallization) solvent system. The synthetic attempt of **2** in the THF/Et₂O system failed to provide the desired metallacycle product and yielded only the mononuclear complex **1**. The synthesis of compound **2** was conducted in acetonitrile and upon crystallization a CH₃CN molecule was trapped in the crystal lattice as described below in the structural detail.

Crystals of compound **2** were not soluble in CHCl₃, hexanes, and Et₂O, but were found to be soluble in CH₃CN, MeOH, acetone, THF, and CH₂Cl₂. Several attempts to remove the trapped CH₃CN from the lattice were unsuccessful including recrystallization using a different solvent, gentle heating and lattice perturbation. These studies were aimed at understanding the solvent effect in crystal modulation and the nature of luminescence changes induced due to the presence of the solvent in the lattice. Gentle heating of the crystals at 80°C for seven days did not remove the CH₃CN molecule from the lattice before noticeable changes were seen upon the

degradation of the crystals, where the pinkish color changed to dark purple/black. The dark color is an indication of decomposition in gold compounds. Each day for one week a single crystal was removed from a watch glass that was placed in an oven and analyzed using IR spectroscopic techniques for the presence of the ν_{CN} stretching peak at $\sim 2250\text{ cm}^{-1}$. After seven days of heating the experiment had to cease as the crystals started to turn dark indicating decomposition of the material.

3.3 Structural Studies

The details of the X-ray structural feature of the MBDP ligand were reported recently by our group [38]. The structural feature of the mononuclear (MDBP)AuCl (**1**) has been conducted. Although the details of the x-ray data of this compound has not been finalized to our satisfaction essential parameters of the data indicate that the compound crystallizes in the space group $P2_1/c$ with unit cell parameters of $a = 15.650(3)\text{ \AA}$, $b = 7.4736(12)\text{ \AA}$, $c = 17.493(3)\text{ \AA}$, $\beta = 113.462(5)^\circ$ with $Z = 4$. The structural feature also indicates the lack of any significant aurophilic Au(I)–Au(I) interaction. The Au–P and Au–Cl distances are roughly comparable to the work of Catalano and Horner [39] on 1-methylimidazole diphenylphosphine ligand.

The X-ray structural feature of complex **2** is shown in Figure 1. The crystallographic details are given in Table 1, while selected bond lengths and angles are shown in Table 2. Compound **2** crystallizes in a monoclinic system with a space group of $P2_1/n$ and with four molecules present in the unit cell. The compound features an eight-membered metallacycle ring consisting of two gold, two phosphorus, two nitrogen, and two carbon atoms. The geometry surrounding the gold is close to linear with a P–Au–N bond angle of 178.3° . The dinuclear system shows two gold atoms at a relatively short Au–Au distance of $\sim 2.80\text{ \AA}$. The bond lengths corresponding for the Au–P and Au–N are 2.228 and $2.074\text{ \AA}$, respectively, while the bond angles

for the P-Au-Au, and N-Au-Au are 91.85° and 87.1° , respectively. Figure 2 shows the packing diagram of **2** looking along the b-axis. Although the Au atoms appear to align along this axis in an extended fashion (with Au-Au---Au angle of 173.3°), the packing diagram clearly indicates that only dimeric Au-Au interactions are dominant. The Au-Au distance between the dimeric units is over $14.7 \text{ \AA}$ indicating the absence of any significant intermolecular interaction. Hence, the complex effectively consists of discrete dimeric units with Au-Au separation of $2.808(4) \text{ \AA}$. This contact is relatively short when compared with the aurophilic interaction for the majority of the complexes that show Au-Au contacts of $\sim 3.0 \text{ \AA}$, albeit interactions as small as 2.45 are also known in few instances [40]. The uncoordinated solvent molecules of CH_3CN present in the structure are trapped within the crystal system and occupy the spaces between the discrete dimeric units.

The thermal ellipsoid diagram of the silver analog, **3**, is shown in Figure 3. The packing diagram shown along the a-axis is presented in Figure 4. The structural details are given in Table 1 while a comparison of the bond distances is shown in Table 2. The colorless complex, **3**, crystallizes in the triclinic space group P-1 with an inversion center midway between the silver atoms, making only half of the complex to be crystallographically unique. The asymmetric unit also contains one BF_4^- anion, and two acetonitrile molecules bound to the silver atom. Similar to the gold system, compound **3** features the characteristic metallacycle consisting of the two Ag atoms and two MBDP ligands that close the loop. There are two CH_3CN molecules attached to each of the silver atoms in the dimeric unit, making a roughly distorted tetrahedral assembly around the Ag atom. This suggests that the Ag(I) adduct of this ligand prefers a tetrahedral geometry as opposed to the linear geometry observed for the Au(I) system.

The bond angle of the phosphorous, silver, and the imine nitrogen deviates significantly from linearity as the N(1)-Ag(1)-P(1) angle is only 147.39 (6)°. The N(1)-Ag(1)-N(3), N(1)-Ag(1)-N(4), and P(1)-Ag(1)-N(3) angles are 98.85(19), 99.82, and 96.85(16)°, respectively where N(3) and N(4) correspond to the bonding CH₃CN nitrogen. As was the case in the gold system (**2**), complex **3** also forms discrete dimers with an intramolecular Ag-Ag separation of 3.017 Å suggesting the existence of intramolecular argentophilic interactions [39-44]

As it is evident from the Ag-Ag---Ag angle of 160.9° (Figure 4) the discrete dimeric units are not aligned in an extended fashion and the separation between these units are also about 7.68 Å, albeit half the value for compound **2**. The bond lengths corresponding to the Ag-P, and Ag-N (1) are 2.388, 2.226 Å, respectively (N (1) corresponds to the imine N). The interaction of the Ag atom with the acetonitrile solvent is much weaker, hence the Ag-N bond length is longer by 0.203 Å when compared with that of the imine N. Hence, the Ag-N3, and Ag-N4 bond lengths are 2.502, and 2.429 Å, respectively.

3.4 Structural comparison

Comparison of the two complexes indicate contrasting geometries in Ag(I) versus Au(I) systems. Accumulated data for silver indicates that in the +1 oxidation state, Ag(I) adopts a wide variety of coordination geometries. For example, a 2008 review article indicated that, of all the Ag(I) complexes characterized structurally and stored in Cambridge data search, the two, three, and four coordinated complexes amount to 24.2, 22.7, and 43.9%, respectively while the remaining components consist of five, six and even seven coordinates [45]. This variety of coordination observed for Ag(I) is in part due to the lack of stereo chemical preference that arises from a d¹⁰ configuration. However, distribution of coordination numbers among the d¹⁰ ions

varies with the metal indicating other factors may also play a significant role in influencing the type of coordination. For example, the majority of the Au(I) complexes appear in a linear two-coordinate geometry, while the large majority of Cu(I) complexes prefer tetrahedral four coordinate geometries [46]. In contrast, when compared to Au(I) and Cu(I) systems, the structural geometries in Ag(I) are more evenly distributed among di, tri and tetrakis geometries [45-46]

Several essential attributes have been suggested as causes for the large differences exhibited within the d^{10} ions of Cu(I), Ag(I), and Au(I) systems. Previous studies conducted on homoleptic copper(I), silver(I), and gold(I) complexes with two bisphosphine ligands indicated that while the dppb ligand (1,2-bis(diphenylphosphino)benzene) forms four-coordinate complexes for all three cations [47], the situation with the POP (2-(diphenylphosphino)phenyl]ether) ligand is different. Both $[\text{Cu}(\text{POP})_2]$ and $[\text{Au}(\text{POP})_2]$ adopt a three coordinate trigonal planar coordination with one uncoordinated phosphorus atom. Steric hindrance caused by the large bite angle of the POP ligand was described as the cause in limiting the coordination on the smaller Cu(I) and Au(I) ions, while the largest among them, Ag(I), was found to adapt a tetrahedral geometry.

Based on a theoretical work, Carvajal et al. [46] have concluded that for the same ligand L the increase in bond distance follows the order $\text{Cu-L} < \text{Au-L} < \text{Ag-L}$, which is consistent with the atomic radius of Au to be smaller than Ag. A similar trend is apparent in the work reported here also where the Au-P bond length of 2.228 Å (Table 2) is smaller by 0.16 Å than the 2.388 Å obtained for the Ag-P bond. Similarly, the Au-N bond is smaller by 0.15 Å when compared with the Ag-N bond length. The weak nature of the silver-ligand bond [48] and the resulting weaker M-L interactions and the crystal packing forces were considered to have a greater influence on

the geometry. These observations on Ag contrast the linear geometry preferred for Au(I) [44, 49].

3.5 Spectroscopic studies

3.5.1 NMR and vibrational studies

Several spectroscopic techniques were used to characterize the complexes including NMR, and IR studies. For the mononuclear compound **1**, the ^1H NMR spectrum collected in CDCl_3 has a similar profile with that of the ligand with peaks at 3.98 (s, 1H), 7.33 – 7.54 (m, 5H), 7.58 – 7.60 (m, 6H), and 7.70 – 7.83 (m, 5H). The $^{31}\text{P}\{^1\text{H}\}$ NMR revealed a single peak at 14.59 ppm.

For compound **2**, due to solubility choice the NMR data were collected using the deuterated solvents CD_3CN or DCM. The ^1H NMR spectrum has a similar profile with that of the ligand and compound **1**. The ^{31}P NMR revealed a single peak at 27.9 ppm which is significantly different from that of the ligand as well as the mono coordinated gold (I) adduct, **1**. The ^{31}P NMR is ~ 53.5 ppm down-field from the ligand and ~ 13.3 ppm down-field from the mononuclear species, **1**.

The Ag(I) complex, **3**, was also characterized using ^{31}P and ^1H NMR in CD_3CN and CDCl_3 at room temperature. The ^{31}P NMR data provided a single broad peak at -1.66 ppm while using the standard phosphoric acid. Previous reports [9, 11, 50-51] of ^{31}P NMR data for silver phosphine complexes have shown broad peaks similar to the one found in complex **3**. The broad feature is presumably due to the dynamic behavior of the ligand scrambling reactions. A very similar NMR behavior of a dinuclear silver complex was published very recently [52]. The ^1H NMR was in a similar range with that of the ligand apart from small shifts. The CH_3CN signal appears as a sharp peak at 2.15 ppm.

3.5.2 Absorption and Photoluminescence Studies

In Figure 5 is shown the absorption spectrum of the MBDP ligand compared with that of compounds **1**, **2**, and **3**. The compounds have somewhat a similar profile with that of the ligand with only slight difference between them. A strong band is evident ~200 nm in all cases. In addition, the compounds have detailed features in the 250-320 nm spectral range. The ligand, compound **1**, and **3** show very similar features in this region with a broad band at ~290 nm accompanied by a shoulder at 299-301 nm. In addition, a broader peak ~268 nm is also evident. Compound **2** displays a slightly different profile in this spectral region where a more defined and sharper band is dominant at 278 nm with a broad hump around 294 nm. The molar extinction coefficients in all systems are $> 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, hence the transitions can be assigned to the spin allowed $\pi \rightarrow \pi^*$ within the ligand in all the systems, although the shift and intensity in **2** might indicate some involvement of the metal orbitals in influencing the electronic transition.

In Figure 6, is shown the photoluminescence spectra of the ligand. The blue spectrum corresponds to the excitation profile where the most intense band maximizes at 311 nm. The emission spectrum, although highly structured, shows a broad feature centering at ~445 nm upon excitation at 311 nm. Several vibronic features are evident in the 240 to 580 nm spectral range. The vibronic components are observed at 354, 372, 389, 404, 418, 427, 449, 471, and 509 nm and an average spacing of $\sim 1020 \text{ cm}^{-1}$. As shown in the supplemental section (Suppl-Fig-2) compound **1** shows similar structured spectral profile to that of the ligand.

Similarly, the gold dimer, **2**, has a photoluminescence profile depicted in Figure 7. These spectra were collected at liquid nitrogen temperature. The excitation spectrum collected while monitoring the emission at 448 nm is shown in the figure (Figure 7, red). The well-defined sharper excitation band in the ligand (at 311 nm, Fig 6) broadens and maximizes at ~330 nm in

the spectrum of **2**, while the longer wavelength region shows several structural features. The emission spectrum of **2** is less structured compared with that of the ligand. However, the band maximum centers around 454 nm which is almost identical in position observed in the free ligand.

The photoluminescence spectrum of the silver dimer, **3**, collected at liquid nitrogen temperature is shown in Figure 8. The excitation spectrum was collected while monitoring the emission at 451 nm. The excitation overall profile, although red shifted to ~320 nm (with a second, smaller broad band at 355 nm) is similar to that observed for the free ligand (Figure 6). The emission spectrum which consists of vibronic components at 423, 449, 475, and 509 with an average spacing of $\sim 1330\text{ cm}^{-1}$ has also a similar profile to that of the ligand.

3.6 Computational Studies

3.6.1 Structural comparison theoretical vs experimental

A summary of the bond lengths and bond angles of the ligand are given in Table 4 comparing the theoretical and the single X-ray crystal structural data of the MBDP ligand. Although the calculated bond distances are slightly longer, the overall geometry of the optimized structural data are in good agreement with the experimental values.

3.6.2 Electronic structures of the MBDP ligand.

The frequency keyword was used to compute the vibrational frequencies for the MBDP ligand with no imaginary frequencies calculated. The GaussView 5 transformed the data to provide an IR spectrum and also automation of the vibrations. Comparison of the frequencies to the collected IR shows comparable data. The vibronic component seen in the luminescence spectra was calculated to correspond to a frequency at $\sim 918\text{ cm}^{-1}$. A calculated peak from the

theoretical work at 911 cm^{-1} was animated to show that there is bending and stretching motion within the 1-methylbenzimidazole ring.

The orbital occupation analysis for this ligand is provided in the supplemental section as Supp-Table 1. The HOMO orbital (# 78) has the largest contribution from the phosphorus atom (P, 53 %), with C (38 %), and N (9 %). The LUMO orbital consists of contributions from the P (8 %), N (15 %), and C (77 %). To fully grasp the molecular orbital contributions, visual representation for the first three LUMO's, and the three HOMO's are shown by orbital correlation diagrams in the *Suppl-Table 1* (last column). These figures clearly indicate that the electronic transitions proceed from the benzimidazole portion of the ligand in the HOMOs to the phenyl rings in the LUMOs. This offers support to conceptualize the transition from $\pi \rightarrow \pi^*$, which is believed to govern the electronic properties of this ligand.

Further analysis using the TD-DFT data of the ligand revealed the presence of a total of three excited states contributing to the calculated theoretical UV-Vis band (Suppl-Figure 3). The first state corresponds to the electronic transition from orbital 78 (HOMO) $\rightarrow$ orbital 79 (LUMO) with total contribution of 98% calculated from the coefficient of the microstate as defined by Gaussian [45] (Supp-Table 1). The second excited state consists of contributions from orbitals 78 (HOMO) $\rightarrow$ 80 (2nd LUMO) and the third excited state with contributions from the orbitals 77 (2nd HOMO) $\rightarrow$ 79 (LUMO). These singly excited states are within the range of comparison to the experimental spectrum seen in Figure 5. The theoretical calculations of the UV-Vis spectrum are consistent with the experimental spectrum, albeit with little shift. For example the peak at 263 nm is similar to that of the experimental 272 nm peak. The calculated ϵ for this peak is $> 10^4\text{ M}^{-1}\text{cm}^{-1}$.

3.6.3 Electronic structures of the MBDP-gold monomer, **1**.

Although treatment of **1** with a relative lower level of theory was employed, it provided useful information while exploring subtle differences in the structure and electronic contributions to the frontier orbitals when comparing it to the ligand, MBDP. The absorption profile of **1** (Figure 5b) shows well resolved peaks at 199, 275, and broad shoulders at 226 and 291 nm. The PL spectrum of **1** also shows structured emission at 414, 429, 453, 483, and 515 nm with an average spacing of 1212 cm^{-1} . These features, while similar to the data obtained for the ligand, show slight differences that necessitated a closer understanding through theoretical work.

The vibronic components (spacing of 1212) in the PL spectrum of **1** can be assigned to the calculated frequency at 1133 cm^{-1} . When this peak was animated in the GaussView software package it displayed bending and stretching from the benzimidazole portion of the ligand with minor H stretching on the two phenyl rings. No motion was observed from the P-Au-Cl bonds. Hence, coupling of the ligand vibration to the electronic transition can be deduced. We viewed the excitation energies from the TD-DFT calculations to obtain the UV-Vis spectrum, shown in the supplemental section as (Suppl. figure 4).

It also provided information regarding the electronic transitions that occurred from the HOMO to the LUMO. The HOMO-LUMO gap, MO 91 and MO 92 respectively, from the theoretical calculations was approximately $40,200\text{ cm}^{-1}$ (249 nm). There were three excited states that should participate in the transition. The first was between MO 90 to MO 92 with a signal at 275 nm. The next was from MO 91 to MO 92 with a signal at 275nm. Finally the third coming from MO 91 to MO 93 and MO 91 to MO 94 with a signal at 265 nm. The last contains two microstate transitions that contribute to the 265 nm. The MO 91 to MO 93 microstate contribution is 96% and the MO 91 to MO 94 contributes 3% to the transition.

When compared to the experimental data there is a slight red shift in the excitation energies. This is likely due to calculated gold participation in these transitions. A better explanation comes from the MO contribution seen in Table 5. The HOMO orbital 91 has mainly contributions from the Au d_{xz} (30 %) and Cl p_z (60 %) whereas the LUMO is totally p-orbital from C and P (p_x --11.5 %; p_y -- 4.5 %, and p_z --48 % remaining percentage given to s-orbital) ligand centered. This infers a charge transfer feature to the π^* orbital of the ligand.

The predicted orbital occupation for these transitions can be seen in the orbital diagrams shown in Table 5 for LUMO+2, LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2 providing pictorial representation for the electronic transition of the gold complex, **1**. Starting with LUMO+2 shows the contributions from the Au, Cl, and phenyl rings. The LUMO+1 donation comes from the benzimidazole and phenyl ring portions of the ligand with small Au participation. The LUMO is 100 % ligand centered whereas the filling of the HOMO is Au-Cl centered. The HOMO-1 is composed of majority Au-Cl contributions with some contribution also. Finally, the HOMO-2 is totally ligand centered. It should be noted that a higher level of theory could provide more details regarding the Au(I) behavior. However, for the purpose of this work both the experimental and theoretical studies have provide support for the conclusion that no metallophilic interaction between either Au(I) or Ag(I) centers are responsible for the luminescence profiles. These arise as a result of ligand-centered excitation and emission.

Conclusion

In this paper the synthesis and structural characterization of the bridging ligand, 1-methyl benzimidazole diphenylphosphine (MBDP) and its coordination with Au(I) and Ag(I) ions is reported as well as the luminescence studies and theoretical DFT calculations. Both metals form binuclear metallacycle complexes with head-to-tail coordination feature. Both the P and N atoms

of the ligand show a stronger interaction with Au(I) than Ag(I) as evaluated from the bond distances. The Au-P and Au-N bonds are shorter by 0.16 and 0.15 Å when compared with the Ag-P, and Ag-N distances, respectively. The gold adduct **2** contains an uncoordinated CH₃CN solvent in the lattice, while two solvent molecules are coordinated to the Ag(I) in **3**. Hence, a linear coordination is exhibited for the gold in **2**, whereas the coordination mode of the metal in **3** reflects a highly distorted tetrahedral geometry. Both compounds show structured emission in the ~450 nm region originating from the ligand based π^* LUMO orbital. This assignment is corroborated with the theoretical time dependent DFT calculation. Although a more direct method such as life-time measurement could have been useful, we have not performed these experiments due to instrumental limitations.

Acknowledgement. Support for this research from National Science Foundation (CHE-0959406) and as well as support from the donors of the Petroleum Research Fund (ACS-PRF) are kindly acknowledged.

Appendix A. CCDC 1443130 and 1443176 contains the supplementary crystallographic data for this paper for compounds **2** and **3**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033).

References

- [1] S.-K. Yip, W.H. Lam, N. Zhu, V.W.-W. Yam, "Synthesis, characterization, structure and luminescence studies of dinuclear gold(I) alkynyls of bis(diphenylphosphino)alkyl- and aryl-amines" *Inorg. Chim. Acta* 359 (2006) 3639.
- [2] S. J. Berners-Price, R.J. Bowen, M.A. Fernandes, M. Layh, W.J. Lesueur, S. Mahepal, M.M. Mtotywa, R.E. Sue, C.E.J. van Rensburg, "Gold(I) and silver(I) complexes of 2,3-bis(diphenylphosphino)maleic acid: Structural studies and antitumour activity" *Inorg. Chim. Acta* 358 (2005) 4237.

- [3] L. Song, S.-Q. Xia, S.-M. Hu, S.-W. Du, X.-T. Wu, "Syntheses, crystal structures and characterization of a series of heterothiometallic gold(I) complexes containing bridging diphosphine ligands" *Polyhedron* 24 (2005) 831.
- [4] V. W.-W. Yam, K.-L. Cheung, S.-K. Yip, K.-K. Cheung, "Synthesis, characterization, structure and luminescence studies of mono-, di- and trinuclear gold(I) phosphine alkynyl complexes" *J. Organomet. Chem.* 681(2003) 196.
- [5] M. I. Garcí'a-Seijo, P. Sevillano, R. O Gould, D. Fernández-Anca, M.E. Garcí'a-Fernández, "Synthesis, reactivity and comparative structural studies on copper(I) and gold(I) halo complexes with tripodal polyphosphines in 1 : 1 metal to ligand ratio. The X-ray crystal structures of three mononuclear neutral compounds" *Inorg. Chim. Acta* 353 (2003) 206.
- [6] A. A. Isab, M. Fettouhi, S. Ahmad, L. Ouahab, "Mixed ligand gold(I) complexes of phosphines and thiourea and X-ray structure of (thiourea-kappaS) (tricyclohexyl phosphine) gold(I)chloride" *Polyhedron* 22 (2003) 1349.
- [7] V.W.-W. Yam, C.-L. Chan, C.-K. Li, K.M.-C.Wong, "Molecular design of luminescent dinuclear gold(I) thiolate complexes: from fundamentals to chemo sensing" *Coord. Chem. Rev.* 216 (2001) 173.
- [8] R. Turpin, A.M. Larssonneur, J. Jaud, P. Castan, "Copper(I) and gold(I) complexes with a phosphorous-sulfur ligand- xray structure of $\text{AuCl}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{SCH}_3]$ " *Inorg. Chim. Acta* 237 (1995) 207.
- [9] F. Bachechi, A. Burini, M. Fontani, R. Galassi, A. Macchioni, B. R. Pietroni, P. Zanello, C. Zuccaccia, "Solid state and solution investigations of derivatives of Group 11 metal ions with 1-benzyl-2-imidazolylidiphenylphosphine (L). Electrochemical behavior of $[\text{M}_2\text{L}_3](2+)$ ($\text{M} = \text{Cu-I; Ag-I}$) and $[\text{AuL}_2](+)$ complexes" *Inorg. Chim. Acta*, 323 (2001) 45-54.
- [10] A. Burini, J.P. Fackler, R. Galassi, T.A. Grant, M. A. Omary, M. A. Rawashdeh-Omary, B. R. Pietroni, R. J. Staples, "Supramolecular chain assemblies formed by interaction of a pi molecular acid complex of mercury with pi-base trinuclear gold complexes" *J. Am. Chem. Soc.* 122 (2000) 11264-11265.
- [11] A. Burini, R. Galassi, S. Ricci, F. Bachechi, A.A. Mohamed, J. P. Fackler, "Mono and Tetranuclear Gold(I) Complexes of Tris(1-benzylimidazole-2-yl)-phosphine" *Inorg. Chem.*, 49 (2010) 513-518.

- [12] A. Burini, B. R. Pietroni, R. Galassi, G. Valle, S. Calogero, "Dinuclear gold(I) and silver(I) derivatives with bridging phosphines containing an imidazole and imidazole ring-X-ray crystal structure of (1-benzyl-2-imidazolyl) diphenylphosphine gold(I) chloride" *Inorg. Chim. Acta*, 229 (1995) 299-305.
- [13] V. J. Catalano, A. L. Moore, *Inorg. Chem.* "Mono-, di-, and trinuclear luminescent silver(I) and gold(I) N-heterocyclic carbene complexes derived from the picolyl-substituted methylimidazolium salt: 1-methyl-3-(2-pyridinylmethyl)-1H-imidazolium tetrafluoroborate" *Chem.* 44 (2005) 6558-6566.
- [14] C. Boehme, J. Uddin, G. Frenking, "Chemical bonding in mononuclear transition metal complexes with Group 13 diyl ligands ER (E = B-Tl) Part X: Theoretical studies of inorganic compounds" *Coord. Chem. Rev.* 1977 (2000) 249-276.
- [15] W. A. Herrmann, V.P.W. Böhm, C. W. K. Gstottmayr, M. Grosche, C. P. Reisinger, T. Weskamp "Synthesis, structure and catalytic application of palladium(II) complexes bearing N-heterocyclic carbenes and phosphines" *J. Organomet. Chem.* 617 (2001) 616-628.
- [16] M. A. Rawashdeh-Omary, M. A. Omary, J. P. Fackler, "Argento-aurophilic bonding in organosulfur complexes. The molecular and electronic structures of the heterobimetallic complex AgAu(MTP)(2) *Inorg. Chimica Acta*, 334 (2002) 376-384.
- [17] M. A. Rawashdeh-Omary, M. A. Omary, J. P. Fackler, R. Galassi, B. R. Pietroni, A. Burini, "Chemistry and optoelectronic properties of stacked supramolecular entities of trinuclear gold(I) complexes sandwiching small organic acids" *J. Am. Chem. Soc.* 123 (2001) 9689-9691.
- [18] F. Bachechi, A. Burini, R. Galassi, A. Macchioni, B. R. Pietroni, F. Ziarelli, C. Zuccaccia, "Solid state and solution structural studies of silver(I) cyclic complexes bearing the (Bzim)Ph₂P ligand" *J. Organomet. Chem.* 593-594: (2000) 392-402.
- [19] V. Peruzzo, C. Pretzsch, F. Tisato, M. Porchia, F. Refosco, C. Marzano, V. Gandin, E. Schiller, M. Walther, H. -J. Pietzsch, "Synthesis and characterization of novel tetrahedral copper(I) complexes comprising tridentate PNP-aminodiphosphines and tetradentate PN(X)P-substituted aminodiphosphines (X = O, S)" *Inorg. Chim. Acta*, 387 (2012) 163-172.
- [20] K. H. Leung, D. L. Phillips, Z. Mao, C. -M. Che, V. M. Miskowski, C. -K. Chan, "Electronic excited states of [Au-2(dmpm)(3)](ClO₄)(2) (dmpm= bis(dimethylphosphine) methane) *Inorg. Chem.* 41 (2002) 2054-2059.

- [21] K. H. Leung, D. L. Phillips, M. -C. Tse, C. -M. Che, V. M. Miskowski, "Resonance Raman investigation of the Au(I)-Au(I) interaction of the $[d\sigma^*p\sigma]$ excited state of $\text{Au-2(dcpm)}_2(\text{ClO}_4)_2$ (dcpm = bis(dicyclohexylphosphine)methane)" *J. Am. Chem. Soc.*, 121 (1999) 4799-4803.
- [22] M. E. Olmos, A. Schier, H. Schmidbaur, "2-(diphenylphosphino)-pyridine as an ambidentate ligand in homo- and hetero-binuclear complexes of copper, silver, and gold" *Naturforsch. B52* (1997) 203-208.
- [23] C. King, J. -C. Wang, J.-C.; Khan, M. N. I.; Fackler, J. P., Jr. "Luminescence and metal-metal interactions in binuclear gold(I) compounds" *Inorg. Chem.* 28 (1989) 2145-2149.
- [24] A. Burini, B. R. Pietroni, R. Galassi, G. Valle, S. Calogero, S. Dinuclear gold(I) and silver(I) derivatives with bridging phosphines containing an imidazole ring x-ray crystal structure of (1-benzyl-2-imidazolyl)diphenyl phosphine gold(I) chloride" *Inorg. Chim. Acta*, 229 (1995) 299-305.
- [25] C. Tejel, R. Bravi, M. A. Ciriano, L.A. Oro, M. Bordonaba, C. Graiff, A. Tiripicchio, A. Burini, "Reversible C-H bond activation of a bifunctional phosphine bridging ligand across two unbonded metal centers" *Organometallics*, 19 (2000) 3115-3111.
- [26] Abdou, H. E., Mohamed, A.A., Fackler, J. P., "Oxidative addition of small molecules to a dinuclear Au(I) amidinate complex, $\text{Au}_2[(2,6\text{-Me}_2\text{Ph})_2\text{N}_2\text{CH}]_2$. Syntheses and characterization of Au(II) amidinate complexes including one which possesses Au(II)-Oxygen bonds" *Inorg. Chem.* 46, (2007) 9692-9699.
- [27] Abdou, H. E., Mohamed, A.A., Fackler, J. P., "Synthesis and X-ray structures of dinuclear and trinuclear gold(I) and dinuclear gold(II) amidinate complexes" *Inorg. Chem.* 44, (2005) 166-168.
- [28] A. Burini, R. Galassi, B. R. Pietroni, G. Ragaini, "Synthesis of dinuclear dicationic heterobridged gold(I) ring derivatives with bis(diphenylphosphines) and bihapto symmetric or asymmetric ligands containing heterocycles: P-31 NMR investigations" *J. Organomet. Chem.* 519, (1996) 161-167.
- [29] H.-X. Zhang, C.-M. Che, "Aurophilic attraction and luminescence of binuclear gold(I) complexes with bridging phosphine ligands: ab initio study *Chem. Eur. J.* 7 (2001) 4887-4893.

- [30] Z. Li, Z. -H. Loh, K. F. Mok, T. S. A. Hor, "Structural, dynamic, and theoretical studies of $[\text{AuPt}_2(\text{PPh}_3)_4(\mu\text{-S})(2\text{-n})(\mu(3)\text{-S})(\text{n})\text{L}][\text{PF}_6]_n$ [$n=1$, $\text{L} = \text{PPh}_3$; $n=2$, $\text{L} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, $(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Fe}$]" *Inorg. Chem.* 39 (2000) 5299-5305.
- [31] A. L. Balch, V. J. Catalano, "Structural motifs in dinuclear d8 metal complexes. Structural and spectroscopic characteristics of an alternative unsymmetrical 3:5 ligand distribution as compared to the symmetrical 4:4 or face-to-face arrangement" *Inorg. Chem.* 31 (1992) 3934-3942.
- [32] Y. Inoguchi, B. Milewski-Mahrla, H. Schmidbaur, H. "2-pyridylphosphanes 2. Ligands for extreme short metal-metal contacts in gold complexes." *Chem. Ber.* 115 (1982) 3085-3095.
- [33] M. A. Rawashdeh-Omary, M. A. Omary, J. P. Fackler, Jr. "Argento-aurophilic bonding in organosulfur complexes. The molecular and electronic structures of the heterobimetallic complex $\text{AgAu}(\text{MTP})_2$ " *Inorg. Chim. Acta* 334 (2002) 376-384.
- [34] R. Uson, A. Laguna, M. Laguna, D. A. Briggs, H.H. Murray, H.H., J. P. Fackler, (tetrahydrothiophene)Gold (I) or Gold (III) Complexes, in *Inorganic Syntheses*. (2007) John Wiley & Sons, Inc. p. 85-91
- [35] S. S. Moore, G. M. Whitesides, "Synthesis and coordinating properties of heterocyclic substituted tertiary phosphines" *J. Org. Chem.*, 47(1982) 1489-1493.
- [36] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009., Gaussian W09. 2009

- [37] M. A. Jalil, T. Yamada, S. Fujinami, T. Honjo, H. Nishikawa, H., "An imidazole-based P-N bridging ligand and its binuclear copper(I), silver(I) and palladium(I) complexes: synthesis, characterizations and X-ray structures", *Polyhedron*, 20 (2001) 627-633.
- [38] D. E. Jenkins, Z. Assefa, "2-Diphenylphosphanyl-1-methyl-1Hbenzimidazole" *Acta Cryst. E* 69 (2013) o1364.
- [39] V. J. Catalano, S. J. Horner, "Luminescent gold(I) and silver(I) complexes of 2-(diphenylphosphino)-1-methylimidazole (dpim): Characterization of a three-coordinate Au(I)-Ag(I) dimer with a short metal-metal separation", *Inorg. Chem.* 42 (2003) 8430– 8438.
- [40] M. D. Irwin, H. E. Abdou, A. A. Mohamed, J. P. Fackler, Jr. "Synthesis and X-ray structures of silver and gold guanidinate-like complexes. A Au(II) complex with a 2.47 angstrom Au-Au distance" *Chem. Comm.* (2003) 2882–2883
- [41] T. C. W. Mak, X. L. Zhao, Q.-M. Wang, G.-C. Guo, "Synthesis and structural characterization of silver(I) double and multiple salts containing the acetylenediide dianion", *Coord. Chem. Rev.*, 251 (2007) 2311–2333.
- [42] S. Sculfort, P. Braunstein, "Intramolecular d(10)-d(10) interactions in heterometallic clusters of the transition metals", *Chem. Soc. Rev.* 40 (2011) 2741–2760.
- [43] M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle, H. H. Patterson, "Crystal structure, electronic structure, and temperature-dependent Raman spectra of $\text{Ti}[\text{Ag}(\text{CN})_2]$: Evidence for ligand-unsupported argentophilic interactions" *Inorg. Chem.* (1998) 37, 1380-1386
- [44] H. Schmidbaur, A. Schier, *Angew. "Argentophilic Interactions"* *Chem. Int. Ed.* 54 (2015) 746–784.
- [45] A. G. Young, L. R. Hanton, "Square planar silver(I) complexes: A rare but increasingly observed stereochemistry for silver(I)" *Coord. Chem. Rev.* 252 (2008) 1346–1386.
- [46] M. A. Carvajal, J. J. Novoa, S. Alvarez, "Choice of coordination number in d(10) complexes of group 11 metals", *J. Am. Chem. Soc.* 126 (2004) 1465-1477.
- [47] A. Kaeser, O. Moudam, G. Accorsi, I. E Séguy, J. Navarro, A. Belbakra, C. Duhayon, N. Armaroli, B. Delavaux-Nicot, J. -F. Nierengarten, "Homoleptic Copper(I), Silver(I), and Gold(I) Bisphosphine Complexes", *Eur. J. Inorg. Chem.* (2014) 1345–1355
- [48] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 1988.

- [49] H. G. Raubenheimer, H. Schmidbaur, "The Late Start and Amazing Upswing in Gold Chemistry" *J. Chem.* 91, (2014) 2024-2036.
- [50] R. Meijboom, R. J. Bowen, S. J. Berners-Price, "Coordination complexes of silver(I) with tertiary phosphine and related ligands" *Coord. Chem. Reviews* 253 (2009) 325-342.
- [51] M. Camalli, F. Caruso, "Crystal and molecular structure of bis(tricyclohexylphosphine) silver(I)nitrate and bis(tricyclohexylphosphine) silver(I)perchlorate; correlation of the structures with the silver-phosphorus coupling constants" *Inorg. Chim. Acta.* 144 (1988) 205.
- [52] Hobbollahi, E.; Himmelsbach, M.; List, M. ; Monkowius, U. "Synthesis and characterization of dinuclear silver(I) complexes with exchangeable nitrile ligands" *Inorg. Chem. Commun.* 71 (2016) 105.

Figure Captions

Figure 1. Thermal ellipsoid diagram of compound **2** at 50% probability.

Figure 2. Packing diagram of the cation portion of compound **2** seen along the b-axis. The BF_4^- anions that occupy the space between the dimeric units are deleted for clarity while the solvent molecules of CH_3CN co crystallized in the lattice are shown.

Figure 3. Thermal ellipsoid diagram of the cation portion of compound **3** at 50% probability

Figure 4. Packing diagram of compound **3**, the silver MBDP dimer, where the BF_4^- anions are deleted for clarity.

Figure 5. Comparison of the absorbance of: a) the MBDP ligand; b) Compound **1**; c) Compound **2**; and d) Compound **3**. Spectral baseline are shifted for clarity. All spectra were collected in acetonitrile solvent.

Figure 6. The PL spectra of the MBDP ligand in the solid state. a) Excitation spectrum monitored at 445 nm, and b) Emission spectrum upon excitation at 311 nm

Figure 7. Excitation (red) spectrum monitored at 448 nm; and emission spectrum excited at 337 nm (right) of compound **2**. Spectra were collected in the solid state at room temperature.

Figure 8. Excitation (red) and Emission (blue) spectra of the silver complex, **3**. Spectra were collected in the solid state at room temperature.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 5

Figure 5

Figure 6

Figure 5

Figure 7

Figure 8

Figure 8

Table 1: Crystallographic Data of the MBDP based Au and Ag compounds **2**, and **3**

Empirical formula	C ₂₂ H ₂₂ AuBF ₄ N ₃ P(2)	C ₄₈ H ₄₈ Ag ₂ B ₂ F ₈ N ₈ P ₂ (3)
Formula weight	643.17	1188.24
Temperature (K)	200(2)	200(2)
Crystal system	Monoclinic	triclinic
Space group	P2 ₁ /n	P -1
Unit cell dimensions		
a (Å)	8.9993(8)	10.5423(10)
b (Å)	19.6166(18)	10.7638(10)
c (Å)	13.4484(12)	12.3530(12)
$\alpha(^{\circ})$	90	88.592(3)
β	$\beta = 100.966(2)$	73.097 (3)
γ	90	84.422(3)
V (Å ³)	1470.8(4)	1334.8(2)
Z	4	1
Density(calc) g/cm ³	1.833	1.478
Absorption coefficient mm ⁻¹	6.427	0.862
Reflections collected	20345	12591
Independent reflections R(int)	4076 (0.0548)	4657(0.0421)
Data / restraints / parameters	4076 / 0 / 291	4657/0/320
Goodness-of-fit on F ²	0.981	1.114
Final R indices	R1 = 0.0264,	0.0337
[I > 2sigma(I)]	wR2 = 0.0635	0.0929
Largest diff. peak and hole e Å ⁻³	1.225 and -0.808	0.874 and -0.425

Table 2: Comparison of selected bond distances in compounds **2** and **3**.

Compound, 2	(Å)	Compound, 3	(Å)
Au1 - Au2	2.808(4)	Ag1 - Ag2	3.017
Au1 - P1	2.228(3)	Ag1 - P1	2.388
Au1 – N2	2.074(4)	Ag1 –N1	2.226
		Ag1 –N3	2.502
		Ag1 –N4	2.429
P1-C1	1.805(5)	P1 – C1	1.821
P1-C9	1.814(5)	P1 - C8	1.818
P1-C15	1.836 (5)	P1 - C12	1.812

Table 3: Selected bond angles for 2 and 3

Compound 2	Bond Angle (°)	Compound 3	Bond Angle (°)
N2-Au1-P1	178.31(11)	N1-Ag1-P1	147.39(6)
N2-Au1-Au2	87.08(11)	N1-Ag1-N4	99.82(11)
P1-Au1-Au2	91.86(3)	P1-Ag1-N4	109.91(10)
C15-P1-Au1	114.81(17)	N1-Ag1-N3	98.85(10)
C9-P1-Au1	112.46(18)	P1-Ag1-N3	96.03(8)
C1-P1-Au1	108.70(17)	N4-Ag1-N3	86.61(13)
C6-N2-Au1	122.80(3)	N1-Ag1-Ag2	85.63(6)
C1-N2-Au1	130.10(3)	P1-Ag1-Ag2	80.72(2)
		N4-Ag1-Ag2	91.33(9)
		N3-Ag1-Ag2	175.33(8)

Table 4: Comparison of structural features from the X-ray crystal structure and theoretical data of the MBDP ligand

	X-ray Crystal Data	Theoretical Data
Bond Angle (°)		
C9-P1-C15	103.70(8)	102.24327
C15-P1-C1	99.42(8)	101.86529
C9-P1-C1	100.85(8)	101.86318
N1-C1-P1	125.23(15)	121.13343
N2-C1-P1	122.6(3)	127.16869
Bond Length (Å)		
P1-C9	1.8304(19)	1.89147
P1-C1	1.8321(19)	1.83736
P1-C15	1.823(2)	1.89146
N1-C1	1.394(2)	1.40198
N2-C1	1.312(2)	1.33735

Table 5

Table 5: Partial Molecular Orbital Contributions in the Ground State of compound **1**

Contributions (%)				Component (%) Contributions			
Orbitals	Cl	Au	Ligand	Cl	Au	Ligand	
94	5	15.63	79.37	1.42s, 3.58p _x	11.19s, 3.17p, 3.21p	3.49s 21.77p _x 16.32p _y 37.79p _z
93		2.29	97.71		2.29s	11.41s 20.04p _x 49.71p _y 16.55p _z
92			100			11.52s 4.50p _x 11.7p _y 72.28p _z
HOMO-LUMO gap							
91	69.29	30.7		69.29p _z	30.70d
90	77.17	16.54	6.28	35.29p _x 41.88p _y	16.54d	6.28s
89			100			100p _z