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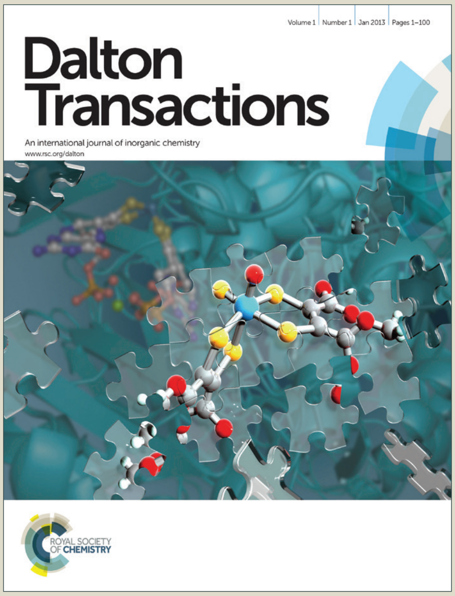

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Gold(I) complexes of bisphosphines with bis(azol-1yl)methane backbone: Structure of a rare dinuclear gold(I) complex [$(Au_2Cl)\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}_3Cl$]

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Gold(I) complexes of bisphosphines assembled on the bis(azol-1-yl)methane platform viz: bis(2-diphenylphosphinoimidazol-1-yl)methane (**1**), bis(5-diphenylphosphinopyrazol-1-yl)methane (**2**), bis(5-diphenylphosphino-1,2,4-triazol-1-yl)methane (**3**) have been described. Reactions of two equivalents of bisphosphines **1-3** with Au(SMe_2)Cl produced dinuclear complexes [$(AuCl)_2(\mu\text{-}P^\wedge P)$] (**4–6**) with Au---Au distances around 3.13 Å. Similar reactions of bisphosphines **1** and **3** in 1:1 molar ratios yielded chelate complexes **7** and **9**, whereas the ligand **2** formed a rare tetracoordinated digold(I) complex [$(Au_2Cl)\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}_3Cl$] (**8**) along with both chelate and binuclear complexes. The complex **8** was also prepared in good yield in 1.5:1 reaction. The structures of complexes **4**, **5** and **8** have been confirmed by single crystal analysis.

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Introduction

The chemistry of d^{10} metals in general and of $\mathrm{Au^I}$ in particular is of considerable interest due to their structural diversities, rich photo-physical properties,[1-5] catalytic[6,7] and biological applications.[8-13] The effective secondary intra- and inter-molecular metal–metal interactions have significantly diversified the structural chemistry of $\mathrm{Au^I}$ with the formation of several interesting molecules and supramolecular architectures.[14-16] These interactions play key role in molecular aggregation both in the solid state and also in solution,[15,17] and also influence greatly the photo-chemical and photo-physical properties of $\mathrm{Au^I}$ complexes. $\mathrm{Au^I}$–$\mathrm{Au^I}$ interactions are observed with interatomic distances typically in the range of 2.7 Å and 3.3 Å, which is shorter than the sum of the van der Waals radii.[16] As the $\mathrm{Au^I}$–$\mathrm{Au^I}$ distance has a direct influence on the luminescence of $\mathrm{Au^I}$ compounds, the best ways to enhance these contacts is by using short bite bidentate ligands which can bring the metal ions in close proximity.[16,18-20] This methodology has been widely employed in the synthesis of numerous $\mathrm{Au^I}$ compounds.

The coordination chemistry of $\mathrm{Au^I}$ is dominated by complexes with linear geometry having coordination number two,[21,22] with few examples of trigonal planar and tetrahedral complexes particularly with phosphine ligands (Chart 1).[10,23-25] The majority of these complexes are based on mono-, bi- or tridentate phosphine ligands, as $\mathrm{Au^I}$ has much higher affinity towards soft donor atoms compared to hard nitrogen and oxygen based ligands. The tetrahedral four coordinate $\mathrm{Au^I}$ complexes of bisphosphines have been employed in chemotherapeutic studies and in the treatment of arthritis.[10,22,26] Imidazole based phosphines are bifunctional ligands having P and N as donor atoms. Transition metal chemistry of imidazole based phosphines is extensive[27,28] due to their effectiveness in various catalytic reactions[29-32] and in biological activities.[10,11] Despite a large number of $\mathrm{Au^I}$ complexes with different monophosphine ligands based on five membered heterocyclic ring being studied, to the best of our knowledge there are no reports on Au^{I} complexes of five membered heterocycle based bisphosphines. This prompted us to study the reactions of bis(2-diphenylphosphinoimidazol-1-yl)methane (**1**), bis(5-diphenylphosphinopyrazol-1-yl)methane (**2**), bis(5-diphenylphosphino-1,2,4-triazol-1-yl)methane (**3**) with Au(SMe$_2$)Cl. As a continuation of our interest in Au^{I} complexes with P/N type ligands,[33-35] herein we report the synthesis and structural characterization of mono and dinuclear Au^{I} complexes including a novel dinuclear gold complex containing both chelating and bridging bisphosphine ligands.

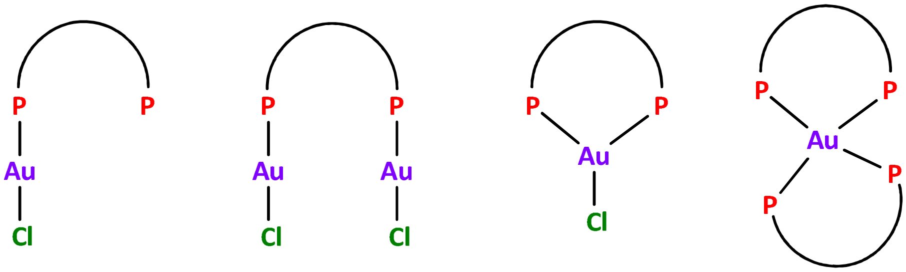
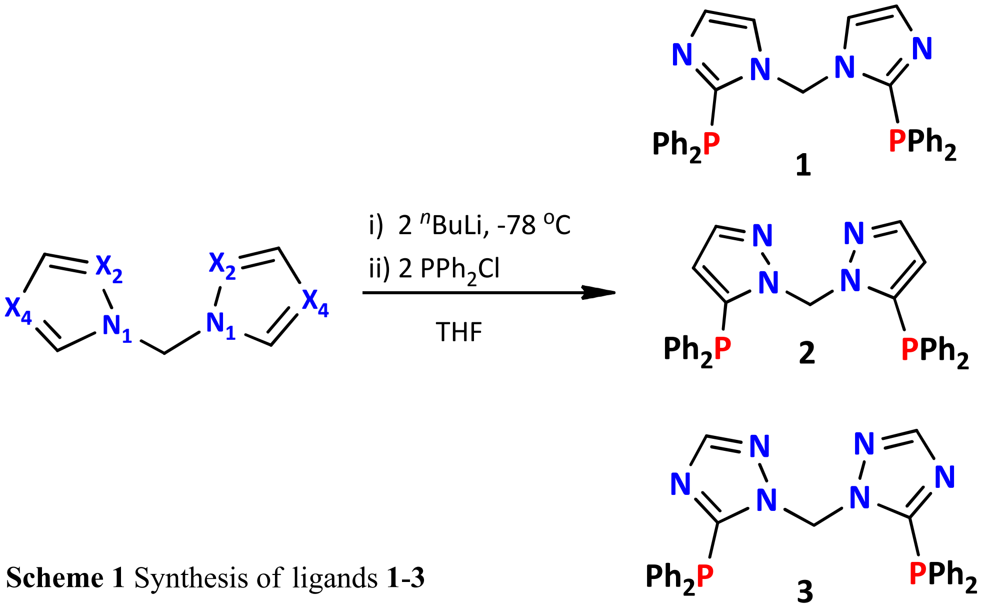


Chart 1 Coordination modes of gold(I) with bisphosphines

Results and discussion

Synthesis of bis(5-diphenylphosphino-1,2,4-triazol-1-yl)methane (3)

Bis(5-diphenylphosphino-1,2,4-triazol-1-yl)methane (**3**) was synthesized by treating bis(1,2,4-triazol-1-yl)methane with two equivalents of ^{n}BuLi in THF at −78 °C followed by the addition of two equivalents of chlorodiphenylphosphine in 63% yield as shown in scheme 1. The bisphosphine ligands: bis(2-diphenylphosphinoimidazol-1-yl)methane (**1**) and bis(5-diphenylphosphinopyrazol-1-yl)methane (**2**) were synthesized according to the reported procedure.[36] The $^{31}P\{^{1}H\}$ NMR spectrum of ligand **3** displayed a single resonance at −34 ppm and the protons of the CH$_2$ linkage in the ^{1}H NMR spectrum showed a triplet at 6.84 ppm with a $^{4}J_{PH}$ coupling of 2 Hz. The $^{13}C\{^{1}H\}$ NMR spectrum of **3** showed CH$_2$ resonance at 59.5 ppm. The bisphosphines **1−3** are potential hemilabile ligands due to their ability to place the other two very different donor atoms in close proximity to the metal atom. Also the exocyclic phosphine arms appended on nitrogen heterocycles can move around easily due to the free rotation around the methylene bridge and will influence their ability to achieve chelating or bridging modes of coordination.



Scheme 1 Synthesis of ligands **1-3**

Gold(I) complexes of ligands **1-3** have been prepared by reacting Au(SMe$_2$)Cl with appropriate phosphine ligands. The reactions of **1–3** with two equivalents of Au(SMe$_2$)Cl resulted in the formation of dinuclear complexes [Au$_2$(μ-P^P)Cl$_2$] (**4–6**) with bisphosphines showing bridging coordination mode (Chart 1). Reactions of **1** and **3** with one equivalent of Au(SMe$_2$)Cl afforded chelate complexes of the type [Au(μ-P^P)Cl] (**7**) and (**9**), whereas similar reaction of **2** yielded a dinuclear complex [Au(μ-P^P)(μ-Cl)(κ^2P^P)$_2$Au]Cl (**8**) containing one bridging and two chelating ligands along with a bridging chloride ion as shown in Chart 2. The reaction of **2** with Au(SMe$_2$)Cl in 1.5:1 molar ratio produced complex **8** in 78% yield.

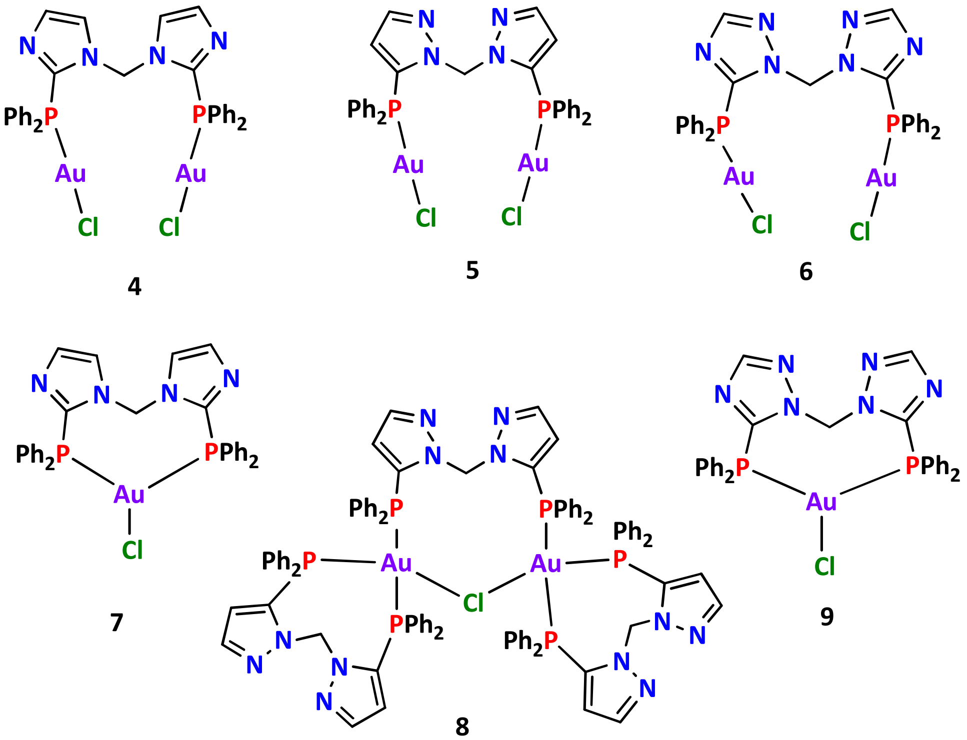


Chart 2 Gold complexes of bis(phosphines) **1-3**

The $^{31}P\{^{1}H\}$ NMR spectra of complexes **4–6** displayed one sharp singlet around 9.7, 10.5 and 10.8 ppm, respectively. In case of **7–9**, broad singlets were observed at 7.5, 10.4 and 5.7 ppm, respectively. Mass spectra of **4–6** showed peaks at *m*/*z* 945.09, 945.07, 947.18 and **7–9** at *m*/*z* 713.13, 713.14, 715.12, respectively, corresponding to $[M{-}Cl]^{+}$. The elemental analysis results are consistent with the two gold centres per ligand in **4–6**, whereas one gold centre per ligand in **7** and **9** and two gold(I) centres per three ligands in **8**. To gain some insights into the formation of complex **8**, solid state structure and its stability in solution, variable-temperature (VT) $^{31}P\{^{1}H\}$ NMR studies in $CDCl_3$ were carried out. A broad singlet was observed at 300 K indicating either the presence of different phosphorus nuclei in **8** which are rapidly equilibrating or a mixture of compounds with very similar chemical shifts. On cooling to 273 K, the broad singlet splits into a doublet and a triplet with a 2:1 intensity ratio thus confirming the presence of complex **8** in the solution (Figure 1). Further, two more singlets were also observed corresponding to the dinuclear complex $[(AuCl)_2\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}]$ (**5**) which shows a sharp peak around 10 ppm and a mononuclear chelate complex $[(AuCl)\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}]$, formed during the course of the reaction. The chelate complex detected at low temperature was similar to the complexes **7** and **9**, obtained during the 1:1 reaction of $Au(SMe_2)Cl$ with bisphosphines **1** and **3**, respectively. NMR tube reaction carried out by taking bisphosphine **2** and $Au(SMe_2)Cl$ in 1.5:1 ratio in $CDCl_3$ also showed initial formation of both chelate and binuclear complexes which eventually resulted in the formation of complex **8**. The structures of **4**, **5** and **8** were confirmed by single crystal X-ray analysis.

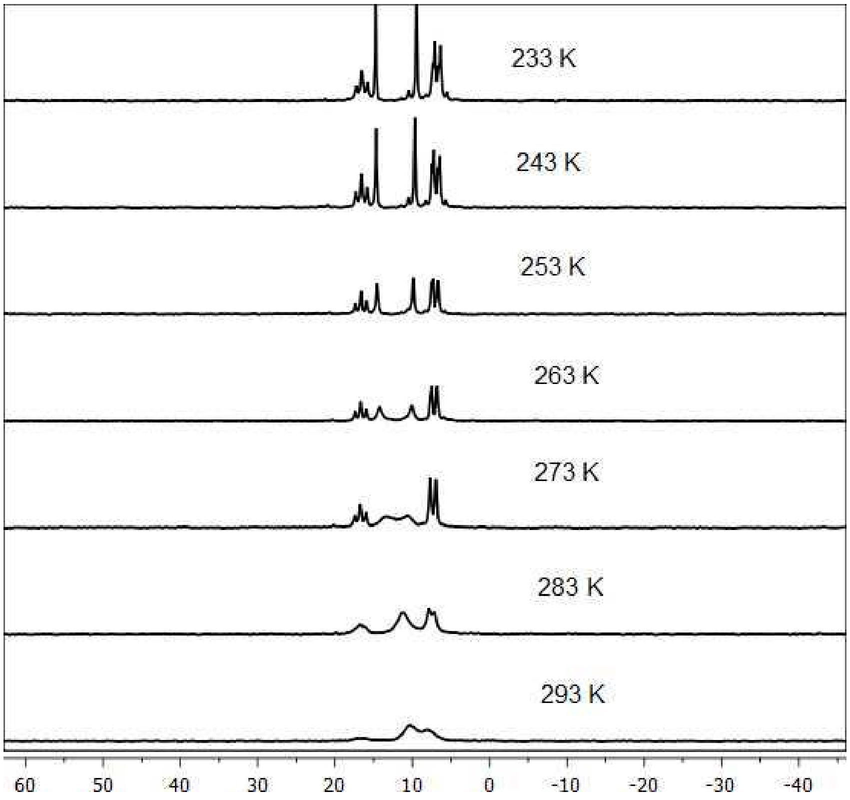


Fig. 1 Variable temperature $^{31}P\{^1H\}$ NMR spectra of $[(Au_2Cl)\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}_3Cl]$ (**8**) in $CDCl_3$.

Molecular structures of compounds 4, 5 and 8

Perspective views of the molecular structures of compounds **4** and **5** with atom numbering schemes are shown in Figures 2 and 3. The selected bond lengths and bond angles are given in Tables 1 and 2. The crystals of the complexes suitable for X-ray diffraction were obtained from dichloromethane-diethyl ether mixture.

In both the complexes, ligands exhibit bridging coordination mode. Both the complexes show intramolecular Au···Au interaction with Au···Au separations of 3.1365(5) Å and 3.1309(2) Å, respectively. The P–Au–Cl moieties are almost orthogonal to each other. The P–Au–Cl bond angles in both the complexes [**4**, 170.25(3)° and **5**, 173.60(3)°] are smaller than those in [PPh_3AuCl][37] (179.68°), [(dpim)AuCl][1] (178.82°) [dpim = 2-diphenylphosphino-1-methyl imidazole] and [(dpBzim)AuCl][38] (175.13°) [dpBzim = 1-benzyl-2-imidazolyl)diphenylphosphine] due to the intramolecular gold-gold interaction, which deviates gold(I) coordination environment from linearity. The P···P distance in **5** increases by 0.7 Å upon coordination compared to the corresponding ligand **2**, whereas it remains almost unchanged in **4** with respect to ligand **1**. The Au1–P1 [2.2429(9), 2.2308(8) Å], Au2–P2 [2.2373(10), 2.2319(7) Å] bond distances are almost identical and fall in the range typical of analogous Au^I complexes containing various bisphosphines.[21] However, Au–P bond distances are longer than the same found in [(dpim)AuCl, 2.227(6) Å]. The average P–C bond distances in case of **4** and **5** are nearly the same and compare well with the P–C bond distances in [(dpim)AuCl]. The Au1–Cl1 [2.3018(9), 2.2812(8) Å] and Au2–Cl2 [2.31365(5), 2.3025(7) Å] bond distances are longer than Au–P bond distances and fall within the expected range for the other related phosphine gold(I) halide complexes.

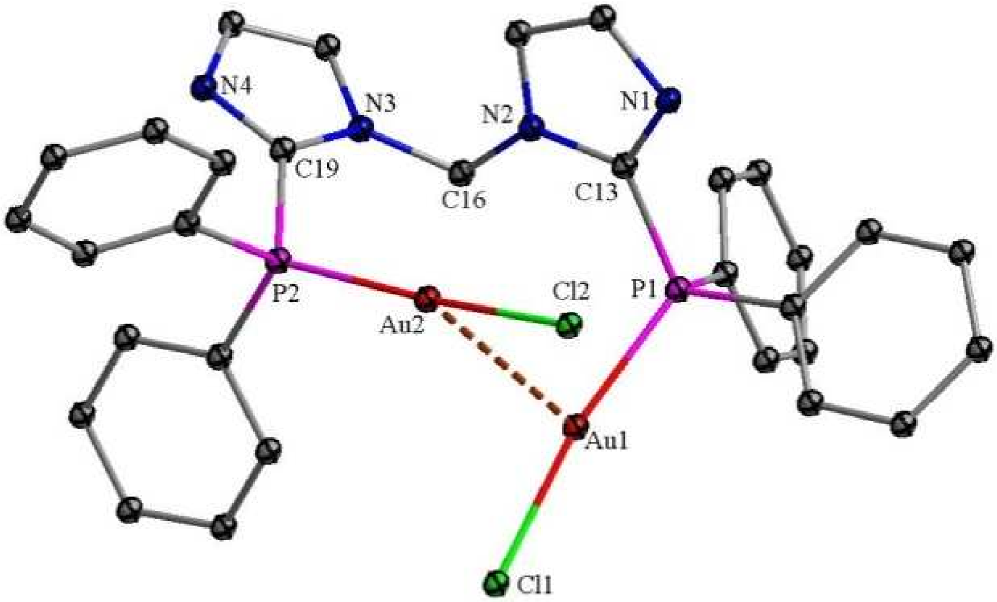


Fig. 2 Molecular structure of $[(AuCl)_2\{CH_2(1,3\text{-}C_3H_2N_2PPh_2)_2\}]$ (**4**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

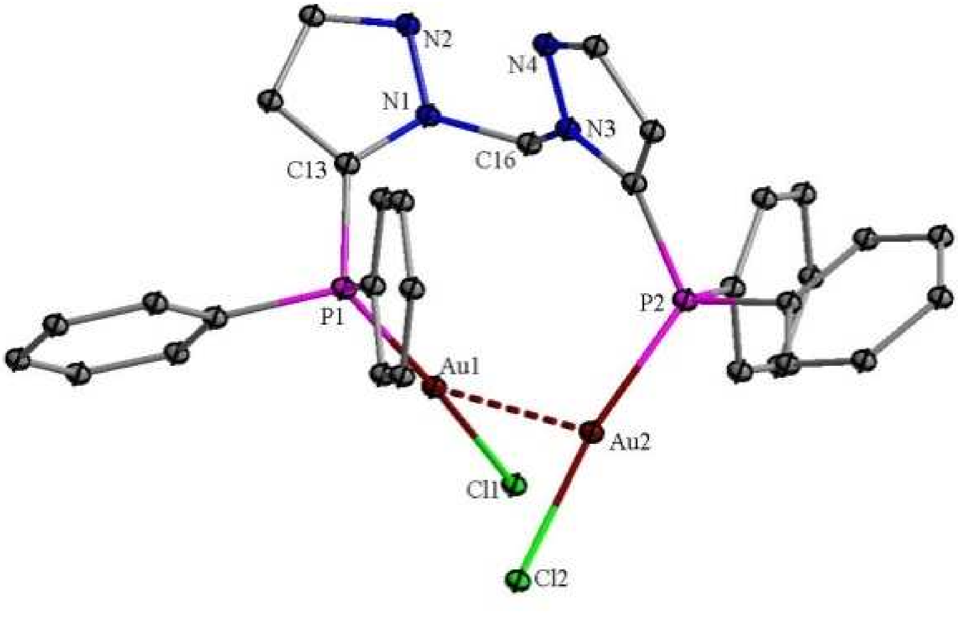


Fig. 3 Molecular structure of $[(AuCl)_2\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}]$ (**5**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

The X-ray quality crystals of **8** were grown from CH_2Cl_2/Et_2O and the molecular structure of **8** is shown in Figure 4. The tetracoordinated Au^I complexes reported in the literature are usually mononuclear with Au^I atom coordinated by two bisphosphine ligands. There is only one example of a binuclear tetrahedral Au^I complex featuring a planar rhombic "$Au(\mu$-$X)_2Au$" core with two bisphosphine ligands coordinated in a *trans*-fashion.[39] There are no reports of dinuclear Au^I complexes of the type **8**, but few analogous dicationic Ag^I complexes of bisphosphines have been reported.[40-42] So it would be interesting to compare the structure of **8** with analogous Ag^I complexes viz: $[Ag_2(\mu\text{-dppm})_3][NO_3]_2$ (**I**),[40] $[Ag_2(\mu\text{-dpmt})_3][BPh_4]_2$ (**II**)[41] and $[Ag_2(\mu\text{-dppf})(dppf)_2][PF_6]_2$ (**III**)[42] (Chart 3). In the case of first two complexes, a triply bridging skelton is found with the phosphorus atoms arranged around the Ag^I atom either in staggered or eclipsed conformations. While in $[Ag_2(\mu\text{-dppf})(dppf)_2][PF_6]_2$ due to the bulky dppf, both chelating and bridging coordination modes have been observed. Complex $[Au(\mu\text{-P^P})(\mu\text{-Cl})(\kappa^2\text{P^P})_2Au]Cl$ (**8**) contain two Au^I atoms bridged by one chloride ion and ligand **2**, which resulted in the formation of a nine membered ring. Each Au^I atom is further coordinated by bisphosphine **2** in a chelating fashion. Thus each Au^I atom adopts a tetrahedral geometry with mean P–Au–P and P–Au–Cl bond angles of 105.106°. The P1–Au1–P2 and P5–Au2–P6 angles are 106.23(13)° and 110.32(14)° with the chelate rings adopting boat conformation. The out of plane distance of Au^I atoms from the P_3 units is about 0.29 Å. The P1···P2 and P5···P6 distances are of 3.845 and 4.143 Å, respectively. These features are analogous to those found in free ligand (P···P = 4.002 Å) indicating that only slight distortion occurs upon coordination of Au^I atom in a chelating manner.

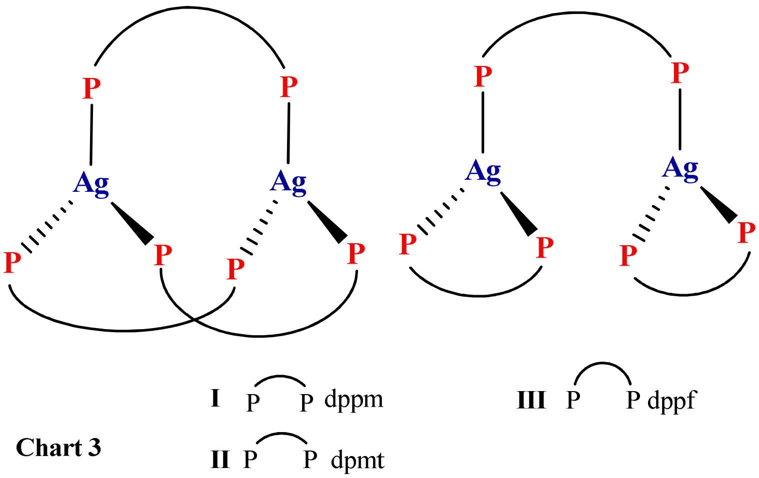


Chart 3

The examination of the crystal structure further reveals the existence of intramolecular C–H···Cl [C47–H47···Cl1= 2.7209 Å, 116°; C16–H16···Cl1= 2.7093 Å, 144.4° and C78–H78···Cl1= 2.5493 Å, 152°] contacts between the chloride ion and one of the CH_2 protons in each bisphosphine, which distorts the Au1–Cl–Au2 bond angle [164.06(14)°]. The Au–P (2.381(4), 2.429(4), 2.356(4) Å), Au2–P (2.357(4), 2.390(4), 2.381(4) Å) bond distances are longer than those in two coordinated gold(I) complexes **4** and **5**, but are comparable to those found in other four coordinated gold(I) complexes containing bisphosphine ligands.[43,44] Further the Au1–P3 and Au2–P4 (2.356(4) Å and 2.357(4) Å) bond distances of the bridging bisphosphine ligand are quite shorter than the Au1–P1/P2 and Au2–P5/P6 bond distances of the chelating ones indicating stronger bonding interaction of the bridging bisphosphine with the gold(I) centres. The Au1–Cl1 (2.849(4)) and (Au2–Cl1 2.819(3) Å) bond distances are longer than the same in two coordinate gold(I) complexes **4** and **5**, indicating weak bonding interaction between the gold(I) and bridging chloride anion. The Au---Au separation in **8** is 5.613 Å.

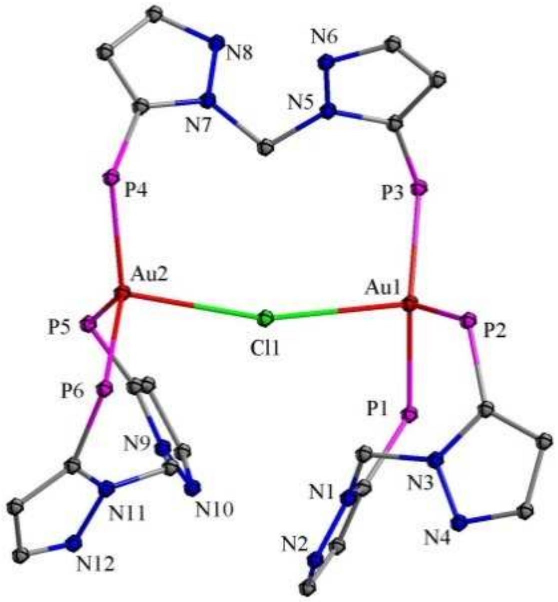


Fig. 4 Molecular structure of [$(Au_2Cl)\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}_3Cl$] (**8**). Thermal ellipsoids are drawn at 50% probability level. Phenyl rings on phosphorus and hydrogen atoms have been omitted from clarity.

Conclusions

In summary, we have reported the synthesis of a geometrically rare dinuclear complex with a chloro bridge and each Au^I is coordinated by large bite bis(azol-1-yl)methane derived bisphosphine ligands exhibiting both chelating and bridging modes of coordination. This molecule is interesting because the intramolecular aurophilic interactions have been blocked due to the chloro-bridge which keeps the two Au^I atoms at a longer distance. If there is a way to cleave Au—Cl—Au bridge reversibly, it may be an ideal candidate to study the aurophilic interactions in such molecules with some application. Further work in this direction is in progress.

EXPERIMENTAL

General Considerations All manipulations were performed in oven-dried glassware using standard Schlenk techniques under nitrogen atmosphere. Solvents were dried under standard conditions. Bis(azol-1-yl)methane,[45] bis(2-diphenylphosphinoimidazol-1-yl)methane[36] (**1**), bis(5-diphenylphosphinopyrazol-1-yl)methane[36] (**2**) and Au(SMe$_2$)Cl[46] were synthesized according to the reported procedure. Other chemicals were obtained from commercial sources and purified prior to use.

Instrumentation The NMR spectra were recorded at the following frequencies: 400 MHz (^{1}H), 162 MHz (^{31}P) using Bruker AV 400 and 500 spectrometers. ^{31}P NMR spectra were acquired using broad band decoupling. The spectra were recorded in CDCl$_3$ solutions with CDCl$_3$ as an internal lock; chemical shifts of ^{1}H spectra are reported in ppm downfield from TMS, used as an internal standard. The chemical shifts of ^{31}P{^{1}H} NMR spectra are referred to 85% H$_3$PO$_4$ as an external standard. The microanalyses were performed using Carlo Erba Model 1112 elemental analyser. Mass spectra were recorded using Waters Q-Tof micro (YA-105). The melting points were observed in capillary tubes and are uncorrected.

Synthesis of [CH$_2$(1,2,4-C$_2$HN$_3$PPh$_2$)$_2$] (3)

To 0.58 g of bis(1,2,4-triazol-1-yl)methane (0.6 g, 4 mmol) dissolved in dry THF (50 mL) was added ^{n}BuLi (1.6 M solution in hexane, 5.2 mL, 8.6 mmol) dropwise at −78 °C and the reaction mixture was stirred for 1 h. Chlorodiphenyphosphine (1.8 g, 8.2 mmol) in THF (20 mL) was added dropwise at −78 °C and the reaction mixture was slowly allowed to reach room temperature and was further stirred for 12 h. The solvent was removed under vacuum and the crude product obtained was washed consecutively with petroleum ether, diethyl ether and extracted with dichloromethane. The ^{31}P{^{1}H} NMR spectrum of the crude product showed two peaks corresponding to **3** and oxidized product. Analytically pure **3** was obtained by passing the crude material through a column of silica gel with ethyl acetate as eluent. Yield: 63% (1.3 g, 2.5 mmol). Mp: 165−172 °C. Anal. Calcd for C$_{29}$H$_{24}$N$_6$P$_2$: C, 67.18; H, 4.67; N, 16.21. Found: C, 66.92; H, 4.81; N, 16.58%. ^{31}P{1H} NMR (162 MHz, CDCl$_3$),

δ:−34.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.81 (t, 2H, $^{4}J_{PH}$ = 2 Hz, CH_2), 7.95 (S, 2H, H^3), 7.31−7.48 (m, 20H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$), δ: 59.5 (t, $^{3}J_{CP}$ = 11 Hz), 153.4, 156.9, 128.9, 130.1, 133.2, 134.2. HRMS (ESI): *m/z* = 519.1609 $(M+H)^+$.

Synthesis of [$CH_2(1,3\text{-}C_3H_2N_2PPh_2)_2$] (1)

This was synthesized by the procedure similar to that for **3** using bis(imidazol-1-yl)methane (1.5 g, 10 mmol), ^{n}BuLi (1.6 M in hexane, 13.6 mL, 21.7 mmol) and chlorodiphenylphosphine (4.6 gm, 20.05 mmol). Yield: 67% (3.5 g, 6.8 mmol). Mp: 175−179 °C. Anal. Calcd for $C_{31}H_{26}N_4P_2$: C, 72.09; H, 5.07; N, 10.85. Found: C, 72.01; H, 4.97; N, 10.24%. ^{31}P{1H} NMR (162 MHz, $CDCl_3$), δ: −34.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.6 (t, 2H, $^{4}J_{PH}$ = 3 Hz, CH_2), 7.17 (d, 2 H, $^{3}J_{HH}$ = 1.3, H), 7.05 (d, 2H, $^{3}J_{HH}$ = 1.3 Hz, H), 7.32−7.48 (m, 20H, Ar). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$), δ: 55.7 (t, $^{3}J_{CP}$ = 17 Hz), 146.3, 132.4, 121.6, 134.1, 128.9, 129.6, 134.3. HRMS (ESI): *m/z* = 517.16 (M+1).

Synthesis of [$CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2$] (2)

This was synthesized by the procedure similar to that for **3** using bis(pyrazol-1-yl)methane (0.86 g, 5.8 mmol), ^{n}BuLi (1.6 M solution in hexane, 3.6 mL, 12.5 mmol) and chlorodiphenylphosphine (2.6 g, 11.8 mmol). Yield: 63% (1.9 g, 3.7 mmol). Mp: 192−195 °C. Anal. Calcd for $C_{31}H_6N_4P_2.CHCl_3$: C, 60.44; H, 4.28; N, 8.81. Found: C, 60.34; H, 4.19; N, 8.45%. ^{31}P{1H} NMR (162 MHz, $CDCl_3$), δ: −34.2 (s). ^{1}H NMR ($CDCl_3$), δ: 6.59 (t, 2H, $^{4}J_{HP}$ = 1.5 Hz, CH_2), 5.94 (d, 2H, $^{3}J_{HH}$ = 1.8, H^4), 7.41 (d, 2H, $^{3}J_{HH}$ = 1.8 Hz, H^3), 7.23−7.37 (m, 20H, Ar). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$), δ: 62.4 (t, $^{3}J_{CP}$ = 17 Hz), 140.8, 140.4, 135.3, 133.6, 128.7, 129.3, 134.2. HRMS (ESI): *m/z* = 539.15 (M+Na).

Synthesis of [$(AuCl)_2\{CH_2(1,3\text{-}C_3H_2N_2PPh_2)_2\}$] (4)

A solution of AuCl(SMe$_2$) (23 mg, 0.077 mmol) in CH$_2$Cl$_2$ (10 mL) was added dropwise to a well stirred solution of **1** (20 mg, 0.038 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature with constant stirring. After stirring for 4 h, the solution was concentrated to about 3 mL under vacuum, petroleum ether was added to precipitate compound **4** as a white solid. Analytically pure **4** was obtained by recrystallizing the crude product in a 1:1 mixture of dichloromethane–diethyl ether. Yield: 73% (27 mg), Mp: 193–197 °C. Anal. Calcd for $C_{31}H_{26}Au_2Cl_2N_4P_2 \cdot CH_2Cl_2$: C, 36.05; H, 2.65; N, 5.25. Found: C, 36.36; H, 2.47; N, 5.45%. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$), δ: 9.7 (s). ^1H NMR (CDCl$_3$), δ: 6.76 (br s, 2H, CH$_2$), 7.13 (br s, H^4), 7.26 (s, H^5), 7.51−7.67 (m, 20H, ArH), 5.21 (s, 2H, CH$_2$Cl$_2$). HRMS (ESI): *m/z* = 945.0867 (M−Cl).

Synthesis of [(AuCl)$_2${CH$_2$(1,2-C$_3$H$_2$N$_2$PPh$_2$)$_2$}] (5)

This was synthesized by the procedure similar to that for **4**, using AuCl(SMe$_2$) (34 mg, 0.116 mmol) and **2** (30 mg, 0.058 mmol). Yield: 84% (47 mg). Mp: 182–184 °C. Anal. Calcd for $C_{31}H_{26}Au_2Cl_2N_4P_2$: C, 37.94; H, 2.67; N, 5.71. Found: C, 37.60; H, 2.53; N, 5.43%. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$), δ: 10.5 (s). ^1H NMR (CDCl$_3$), δ: 5.97 (s, 2H, H^4), 6.66 (s, 2H, CH$_2$), 7.47 (d, $^3J_{HH}$ = 1.8 Hz, 2H, H^3), 7.49−7.66 (m, 20H, ArH). HRMS (ESI): *m/z* = 945.0689 (M−Cl).

Synthesis of [(AuCl)$_2${CH$_2$(1,2,4-C$_2$HN$_3$PPh$_2$)$_2$}] (6)

This was synthesized by the procedure similar to that for **4**, using AuCl(SMe$_2$) (34 mg, 0.115 mmol) and **3** (30 mg, 0.057 mmol). Yield: 82% (47 mg). Mp: 179–185 °C. Anal. Calcd for $C_{29}H_{24}Au_2Cl_2N_6P_2$: C, 35.42; H, 2.46; N, 8.55. Found: C, 35.17; H, 2.43; N, 8.84%. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$), δ: 10.8 (s). ^1H NMR (CDCl$_3$), δ: 7.35 (s, 2H, CH$_2$), 7.89 (s, 2H, H^3) 7.5−7.75 (m, 20H, ArH). HRMS (ESI): *m/z* = 947.1868 (M−Cl).

Synthesis of [(AuCl){$CH_2(1,3\text{-}C_3H_2N_2PPh_2)_2$}] (7)

This was synthesized by the procedure similar to that for **4**, using AuCl(SMe_2) (13 mg, 0.044 mmol) and **1** (23 mg, 0.044 mmol). Yield: 75% (27 mg), Mp: 187−190 °C. Anal. Calcd for $C_{31}H_{26}AuClN_4P_2$: C, 49.71; H, 3.50; N, 7.48. Found: C, 49.65; H, 3.32; N, 7.56%. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$), *δ*: 7.5 (br s). ^1H NMR ($CDCl_3$), *δ*: 6.76 (br s, 2H, CH_2), 7.13 (br s, H^4), 7.26 (s, H^5), 7.51−7.67 (m, 20H, ArH). HRMS (ESI): *m/z* = 713.1288 (M−Cl).

Synthesis of [(Au_2Cl){$CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2$}$_3$Cl] (8)

This was synthesized by the procedure similar to that for **7** using AuCl(SMe_2) (17 mg, 0.058 mmol) and **2** (30 mg, 0.058 mmol). The above reaction of AuCl(SMe_2) with 1.5 equivalents of ligand **2** yielded the same complex **8** in 78% yield. Yield: 33% (40 mg). Mp: 197−202 °C. Anal. Calcd for $C_{93}H_{78}Au_2Cl_2N_{12}P_6$: C, 55.45; H, 3.90; N, 8.34. Found: C, 55.37; H, 3.78; N, 8.59%. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$), *δ*: 10.4 (br s). ^1H NMR ($CDCl_3$), *δ*: 5.90 (s, 2H, H^4), 6.68 (s, 2H, CH_2), 7.29-7.61 (m, 20H, ArH).

Synthesis of [(AuCl){$CH_2(1,2,4\text{-}C_2HN_3PPh_2)_2$}] (9)

This was synthesized by the procedure similar to that for **7** using AuCl(SMe_2) (17 mg, 0.057 mmol) and **3** (30 mg, 0.057 mmol). Yield: 73% (32 mg). Mp: 183−186 °C. Anal. Calcd for $C_{29}H_{24}AuClN_6P_2$: C, 46.39; H, 3.22; N, 11.19. Found: C, 46.68; H, 3.20; N, 11.39%. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$), *δ*: 5.7 (br s). ^1H NMR ($CDCl_3$), *δ*: 7.81 (s, 2H, H^3) 7.25−7.43 (m, 22H, CH_2, ArH). HRMS (ESI): *m/z* = 715.1119 (M−Cl).

Crystal structure determination of compounds 4, 5 and 8

Single crystal X-ray structural study of **4**, **5** and **8** were performed at 100–150 K temperature using Bruker Smart APEX CCD diffractometer with Mo-Kα radiation source for **4** and **5** and Bruker D8 VENTURE PHOTON 100 CMOS with Cu-Kα radiation source for **8**. Full spheres of data were collected using a combination of three sets of 400 frames (0.5° width in ω) at $\varphi = 0$, 90, and 180° plus two sets of 800 frames (0.45° width in ω) at $\varphi = -30$, and 210° under the control of the APEX2[47] program suite. The raw data were reduced to F^2 values using the SAINT[48] software, and global refinements of unit cell parameters using 7489−8979 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS).[49] The structures were solved by direct methods, and refined by full-matrix least-squares procedures using the SHELXTL program package.[50,51] Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Crystal data and the details of the structure determination are given in Table 1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1407891 (compound **4**), 1407892 (compound **5**) and 1407893 (compound **8**).

Associated content

Supporting Information

Electronic supplementary information (ESI) available: NMR and crystallographic data CCDC 1407891 (compound **4**), 1407892 (compound **5**) and 1407893 (compound **8**). For ESI and crystallographic data in CIF or other electronic format see DOI:10.1039/x0xx00000x.

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Table 1. Selected Distances (Å) and Angles (°) for Complexes **4** and **5**.

	4	**5**
Au1–P1	2.2429(9)	2.2812(8)
Au2–P2	2.2373(10)	2.2308(8)
Au1–Cl1	2.3018(9)	2.3025(7)
Au2–Cl2	2.31365(5)	2.2319(7)
Au1···Au2	3.1365(5)	3.1309(2)
Cl1–Au1–P1	170.25(3)	173.60(3)
Cl2–Au2–P2	170.27(3)	170.58(3)
Au2–Au1–P1	90.56(2)	96.16(2)
Cl1–Au1–Au2	96.52(2)	90.24(3)
Au1–Au2–P2	113.12(3	99.139(19)
Cl2–Au2–Au1	76.58(2)	89.29(2)

Table 2. Selected Distances (Å) and Angles (°) for Complex **8**.

Bond distances		Bond angles	
Au1–Cl1	2.849(4)	P3–Au1–Cl1	103.57(12)
Au1–P1	2.381(4)	P1–Au1–Cl1	89.89(12)
Au1–P2	2.429(4)	P2–Au1–Cl1	104.96(12)
Au1–P3	2.356(4)	P1–Au1–P2	106.23(13)
Au2–Cl1	2.819(3)	P2–Au1–P3	112.93(13)
Au2–P4	2.357(4)	P3–Au1–P1	133.05(13)
Au2–P5	2.390(4)	P4–Au2–Cl1	107.62(12)
Au2–P6	2.381(4)	P5–Au2–P6	110.32(14)
Au2···Au1	5.891	P4–Au2–P6	119.94(13)
		P5–Au2–Cl1	94.35(12)
		P6–Au2–Cl1	95.88(12)

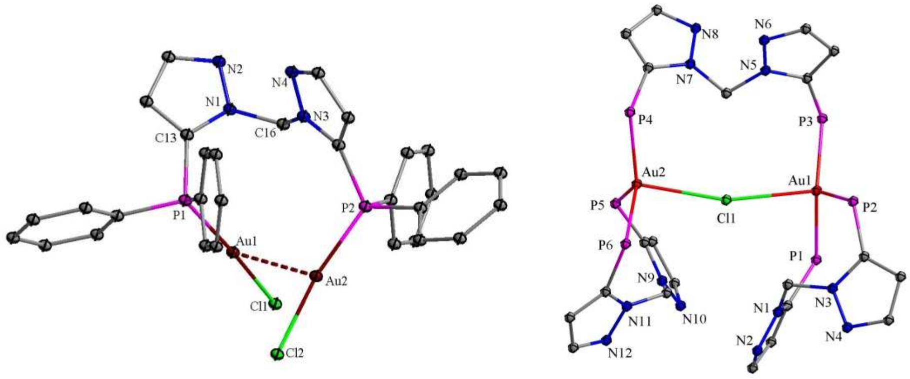
Table 3. Crystallographic data for **4**, **5** and **8**.

	4	**5**	**8**
Empirical formula	$C_{31}H_{26}Au_2Cl_2N_4P_2\cdot CH_2Cl_2$	$C_{31}H_{26}Au_2Cl_2N_4P_2$	$C_{93}H_{78}Au_2ClN_{12}P_6\cdot Cl$
Fw	1066.26	981.33	2014.32
Cryst. System	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca* (no. 61)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a, Å	15.155(2)	10.7505(10)	13.2229(3)
b, Å	17.012(3)	21.136(2)	26.6831(5)
c, Å	26.119(4)	17.2248(16)	24.6194(5)
α, deg	90	90	90
β, deg	92.438(40	97.6160(13)	95.7770(13)
γ, deg	90	90	90
V, A^3	6733.9(18)	3879.4(6)	8642.3(3)
Z	8	4	4
$D_{calc,}$ g cm^{-3}	2.103	1.680	1.548
μ (MoKa), mm^{-1}	9.147	7.798	8.333
F(000)	4032	1848	4008
Crystal size, mm	0.15x0.19x0.26	0.12x0.13x0.24	0.01x0.03x0.08
T(K)	100	150	101
2Θrange, deg	2.0-29.1	2.26-29.2	3.3-59.9
Total no. Reflns	113003	10287	12745
No. Of indep reflns	8941	8979	8762
S	1.04	1.046	1.082
R_1	0.0257	0.0298	0.0839
wR_2	0.0575	0.0575	0.1726

Synopsis for the contents page

Gold(I) complexes of bisphosphines with bis(azol-1yl)methane backbone: Structure of a rare dinuclear gold(I) complex $[(Au_2Cl)\{CH_2(1,2\text{-}C_3H_2N_2PPh_2)_2\}_3]Cl$

Sajad A. Bhat, Joel T. Mague, Maravanji S. Balakrishna



This paper describes the synthesis of gold(I) complexes of bisphosphines based on bis(azol-1-yl)methane *viz* bis(imidazol-1-yl)methane, bis(pyrazol-1-yl)methane and bis(1,2,4-triazol-1-yl)methane.