# Gold(I) Complexes Bearing P∩N-Ligands: An Unprecedented Twelve-membered Ring Structure Stabilized by Aurophilic Interactions

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 75$^{th}$ birthday*

The P∩N-ligands Ph$_2$Pqn, **1**, Ph$_2$Piqn, **2**, Ph$_2$Ppym, **3**, and the As∩N-ligands Ph$_2$Asqn, **4**, Ph$_2$Asiqn, **5**, (Ph = phenyl, qn = 8-quinoline, iqn = 1-isoquinoline, pym = 2-pyrimidine) have been synthesized, the ligands **2** and **5** for the first time. Their ligand properties were probed by the synthesis of gold(I) complexes. Reaction with (tht)AuCl (tht = tetrahydrothiophene) yielded the chlorogold complexes Ph$_2$RP–Au–Cl (R = qn, **6**; iqn, **7**; pym, **8**) and Ph$_2$RAs–Au–Cl (R = qn, **9**; iqn, **10**) in high yields. Further treatment of **7** and **8** with one equivalent of AgBF$_4$ provided the complexes [(Ph$_2$Piqn)Au]BF$_4$, **11**, [(Ph$_2$Ppym)Au]BF$_4$, **12**, and [(Ph$_2$Piqn)Au(tht)]BF$_4$, **14**. For comparison, the previously reported complex [(Ph$_2$Ppy)Au]BF$_4$ (py = pyridine), **13**, was re-investigated. The compounds were characterized by elemental analyses, mass spectrometry and NMR spectroscopy. In addition, the solid-state structures of **2**, **3**, **6**, **7**, **9** – **14** have been determined by X-ray crystallography.

The chloro-gold compounds crystallize in the common rod-like structure known from R$_3$EAuCl (R = aryl, E = P, As) complexes without further aggregation *via* aurophilic interactions. In all cases the phosphine acts as a monodentate ligand. In the solid state compounds **11** – **13** feature an unprecedented cyclic trinuclear aggregation pattern, in which the Au(I) atoms are linearly coordinated by the bridging phosphine ligands forming a cyclic (P–Au–N)$_3$ arrangement. The resulting twelve-membered ring is further stabilized by Au $\cdots$ Au interactions. Due to the presence of these Au $\cdots$ Au contacts, **11** – **13** are emissive in the solid state but not in solution.

*Key words:* Gold(I) Complexes, Phosphines, Arsines, P∩N Ligands, Luminescence, Aurophilic Interactions

## Introduction

Gold in its oxidation state +1 has a rich coordination chemistry with coordination patterns not always predictable. In general, the gold(I) cations are linearly coordinated, but the possibility of an extension to higher coordination numbers by building up intra- or intermolecular gold $\cdots$ gold (aurophilic) interactions often leads to multifarious aggregation patterns. Depending on the steric bulkiness and the electronic properties of the ligands, the weak Au $\cdots$ Au bonding (5 – 10 kcal mol$^{-1}$) gives rise to an aggregation of the gold(I) complexes leading to dimers and oligo-/polymeric arrays [1, 2]. If bidentate ligands are involved, the formation of rings (instead of polymers) is also possible, and aurophilic contacts can determine the favored structure. Furthermore, these aurophilic interactions frequently give rise to phosphorescence in the solid state [3, 4] and in special cases also in solution. Still, there is no clear relationship established between the luminescence properties and the crystallographic Au $\cdots$ Au distances [5]. Recently, Omary *et al.* pointed out that the solid-state phosphorescence energy is more determined by the supramolecular arrangement of the Au(I) complexes than by the shortest Au $\cdots$ Au distances [4]. Some of these highly emissive Au(I) complexes havew been used for the fabrication of organic light-emitting devices (OLEDs) [6, 7].

Further structural options are possible when ambidentate ligands with different electronic properties of the binding atoms are employed. Especially the combination of “soft” (*e. g.* phosphorus, arsenic, sulfur)

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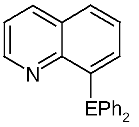
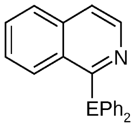


E = P, **1**
As, **4**



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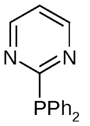
As, **5**



**3**

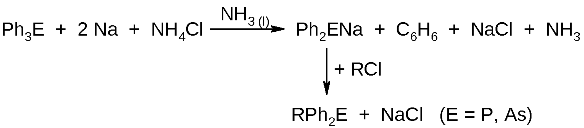
and “hard” (*e. g.* oxygen, nitrogen) donor atoms in one particular ligand opens interesting binding patterns for the “soft” gold(I) center. Among them, P∩N ligands are well established, and several gold(I) complexes have been reported [8–13]. For example, in the complex cations $[(Me_2Ppy)_2Au_2]^{2+}$ (Me = methyl, py = pyridine) and $[(Ph_2Pim)_2Au_2]^{2+}$ (Ph = phenyl, im = methylimidazole) the P∩N ligands act in a bridging manner and thus support short aurophilic interactions [8, 12].

The E∩N ligands (E = P, As) $Ph_2Pqn$, **1**, $Ph_2Ppym$, **3**, and $Ph_2Asqn$, **4**, (qn = 8-quinoline, pym = 2-pyrimidine) were previously prepared [14–19] and used as ligands for the transition metals Fe, Co, Ni, Cu, Ru, Rh, Ir, Pd, and Pt [16, 19–25], and Ru- [26] and Pd-complexes [27, 28] bearing comparable 8-quinoline phosphines (*e. g.*, $Me_2Pqn$, MePhPqn) are also known. Although E∩N ligands constitute an important family of compounds, and their application in catalysis is frequently reported [21, 22, 29–31], the synthesis of $Ph_2Piqn$, **2**, and $Ph_2Asiqn$, **5**, (iqn = 1-isoquinoline) has to our knowledge never been published. Therefore, we became interested in the synthesis and coordination chemistry of the ambidentate ligand systems **1**–**5**, and some of their gold(I) complexes are presented here. Complexes with W(0), Re(I) and Cu(I) will be reported in following publications.

## Results and Discussion

### *Synthesis of the ligands and their Au(I) complexes*

The ligands were prepared in moderate to good yield and high purity by the reaction of *in situ*-generated $Ph_2ENa$ (E = P, As) with the respective aryl chloride RCl in liquid ammonia (Scheme 1) [15]. After evaporation of the solvent and washing of the residue with water the phosphines/arsines were purified by recrystallization from ethanol. Their identity was confirmed by NMR spectroscopy, mass spectrometry and elemental analyses (see Experimental Section). In addition, the solid-state structures of 1-diphenylphosphino-isoquinoline, **2**, and 2-diphenylphosphino-pyrimidine, **3**, were determined by single crystal X-ray diffraction.



$$Ph_3E + 2\,Na + NH_4Cl \xrightarrow{NH_{3\,(l)}} Ph_2ENa + C_6H_6 + NaCl + NH_3 \xrightarrow{+\,RCl} RPh_2E + NaCl \quad (E = P, As)$$

Scheme 1.

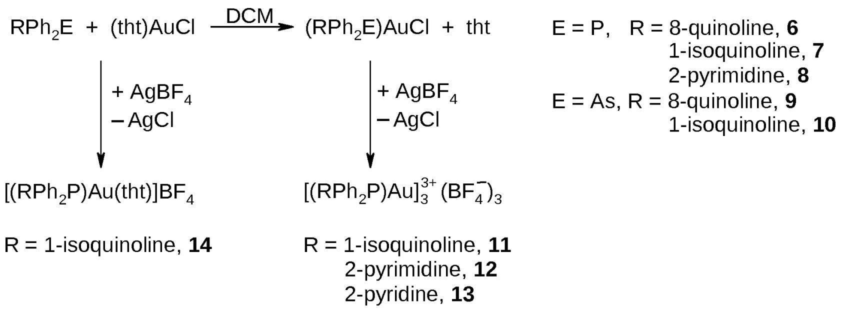
Table 1. $^{31}P\{^1H\}$ NMR chemical shifts of the free phosphine ligands and their gold(I) complexes.

| R | $Ph_2PR$ (ppm) | $(Ph_2PR)AuCl$ | $[(Ph_2PR)Au]BF_4$ |
|---|---|---|---|
| 8-quinoline | −14.34 | 26.89 | – |
| 1-isoquinoline[a] | −7.06 | 28.80 | 28.48 |
| 2-pyrimidine | 1.32 | 35.00 | 36.60 |
| 2-pyridine | −3.41 | 32.66 [8] | 35.15 |

[a] $\delta$P for **14** is 32.17 ppm.

The complexes $(RPh_3E)AuCl$, **6**–**10**, were easily prepared by mixing stoichiometric amounts of (tht)AuCl (tht = tetrahydrothiophene) and the phosphine/arsine ligands **1**–**5** in dichloromethane at ambient temperature (Scheme 2) [32]. Colorless powders were obtained after precipitation with *n*-pentane. Compounds **6**–**10** are air-stable at r. t. and only slightly sensitive to light. They are soluble in polar aprotic solvents such as dichloromethane and acetonitrile. Complexes **7** and **8** were further treated with $AgBF_4$ in order to remove the chloride ligand, and to facilitate the coordination of the weakly binding nitrogen atom of the heteroaromatic moiety. The previously reported complex **13** was prepared by the same procedure [8]. Again, the resulting compounds **11** and **12** are isolated as colorless powders, which are passably stable in the solid state. However, in solution they are sensitive to temperature and light and decompose slowly even at −30 °C. The gold complexes are almost insoluble in dichloromethane, but soluble in acetonitrile and acetone. If the (phosphino)gold chloride **7** is directly reacted with $AgBF_4$, the tht adduct **14** is formed. Treatment of compounds **6** and **9** with $AgBF_4$ resulted in the formation of colloidal gold, and no phosphine/arsine gold(I) complexes could be isolated. Therefore, no further attempts for their preparation were undertaken.

All ligands and complexes furnish expected $^1H$, $^{13}C$ and $^{31}P$ NMR spectra. Upon coordination to the gold atom, the $^{31}P$ NMR signals of the ligands are significantly downfield shifted (Table 1). Compared to the chloro-gold complexes, the $^{31}P$ NMR shifts of **11**–**13** are only slightly affected by the removal of the chloride ligand. Nevertheless, the broadening of the proton signals indicate a ligand scrambling, whereas in the L–Au–Cl compounds these signals are well resolved. Due to the low affinity of nitrogen donor functions towards gold(I) atoms and to the fact that



Scheme 2.

the trinuclear compounds (*vide infra*) are measured in [D$_3$]acetonitrile, which itself is known to be a ligand for metal atoms, it is most likely that the cluster is not conserved in solution, and monomeric species with coordinating solvent molecules are dominant.

## *Structural studies*

### *Ligands*

Single crystals of **2** and **3** suitable for structure determination by X-ray diffraction are obtained upon slow cooling of an ethanolic solution to −35 °C. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with 2 molecules in the unit cell. The nitrogen atom is located opposite to the lone pair of the phosphorus atoms (Fig. 1). In the crystal, the molecules are associated into dimers *via* π-stacking interactions with distances between the isoquinoline moieties of *ca.* 3.5 Å.

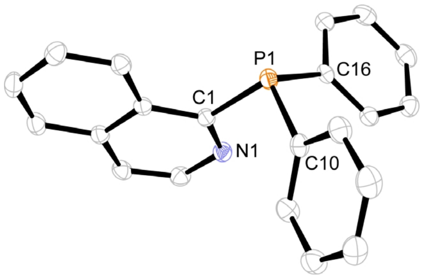


Fig. 1. Molecular structure of **2** (ORTEP; displacement ellipsoids at the 50 % probability level). Selected bond lengths (Å) and angles (deg): P1–C1 1.865(1), P1–C10 1.845(1), P1–C16 1.842(1); C1–P1–C10 101.4(1), C1–P1–C16 101.1(1), C10–P1–C16 102.9(1).

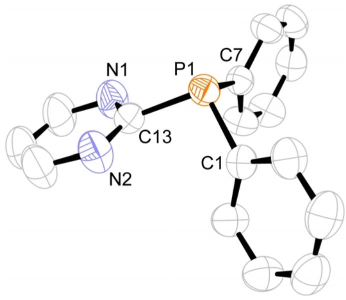


Fig. 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): P1–C1 1.832(3), P1–C7 1.836(3), P1–C13 1.845(3); C1–P1–C7 102.5(1), C7–P1–C13 101.5(1), C1–P1–C13 101.9(1).

Crystals of **3** are monoclinic, space group $P2_1/c$, with 4 molecules in the unit cell. The phosphine molecule has no crystallographically imposed symmetry (Fig. 2). All P–C bond lengths and C–P–C bond angles of both phosphines are very similar and occur in the expected region for aromatic phosphines [33].

### *Gold(I) complexes*

The best studied class of coordination compounds of univalent gold are (phosphino)gold(I) complexes, especially (phosphino)gold(I) chlorides, R$_3$PAuCl [1]. Usually, the gold(I) atoms are linearly coordinated by the phosphorus and halogen atoms forming a neutral complex. Up to now, the only example of a 1 : 1 complex with an ionic structure is [(Ad$_2$BnP)$_2$Au][AuCl$_2$] (Ad = 1-adamantyl, Bn = benzyl) [34]. Single crystals of the gold complexes **6**, **7**, **9**, and **10** were grown from CH$_2$Cl$_2$/Et$_2$O. The arsine complexes **9** and **10** crystallize with half an equivalent of diethyl ether per unit cell. Thus, crystals of the homologous complexes (RPh$_2$E)AuCl (R = quinoline, **6/9** and isoquinoline **7/10**) are not isomorphous (**6**: triclinic, $P\bar{1}$, $Z = 2$; **9**: monoclinic, $P2_1/n$, $Z = 4$; **7**: monoclinic, $C2/c$, $Z = 8$; **10**: monoclinic, $P2_1/c$, $Z = 4$). Nevertheless, the conformations of the gold(I) chloride complexes are very similar, and none of them has crystallographically imposed molecular symmetry (Figs. 3 – 6). The asymmetric units contain one heteroleptic complex L–Au–Cl not associated *via* aurophilic interactions. This result is in agreement with the crystal structures of (triarylphosphine)gold(I) chlorides, which also feature monomeric units [35]. De-

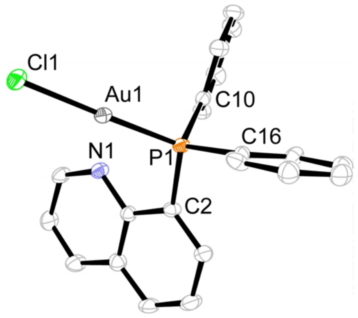


Fig. 3. Molecular structure of **6**. Selected bond lengths (Å) and angles (deg): Au1–P1 2.239(1), Au1–Cl1 2.299(2), P1–C2 1.826(5), P1–C10 1.826(5), P1–C16 1.821(4); Cl1–Au1–P1 173.8(1), Au1–P1–C2 111.7(1), C2–P1–C10 108.2(2).

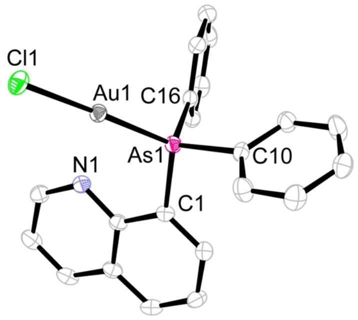


Fig. 4. Molecular structure of **9**. Selected bond lengths (Å) and angles (deg): Au1–As1 2.342(1), Au1–Cl1 2.293(1), As1–C1 1.946(3), As1–C10 1.946(3), As1–C16 1.938(3); As1–Au1–Cl1 178.5(1), Au1–As1–C1 116.1(1), C1–As1–C10 102.8(1).

spite the favorable chelating geometry of the quinoline and isoquinoline group no contacts between the gold and the nitrogen atoms are present, which again shows the low tendency of nitrogen donors to bind to gold(I) atoms [36]. The gold atoms are solely attached to the phosphorus/arsenic atoms with very similar Au–P [**6**: 2.239(1), **9**: 2.238(1) Å] and Au–As distances [**7**: 2.342(1), **10**: 2.345(1) Å]. The Au–Cl distances are only marginally longer in the phosphine complexes compared to the arsine complexes [**6**: 2.299(2), **9**: 2.296(1) *vs.* **7**: 2.293(1), **10**: 2.291(1) Å]. The coordination geometry at the Au atom is linear with P–Au–Cl angles of 173.9(1) (**7**) and 175.2(1)° (**9**) and As–Au–Cl angles of 178.5(1) (**7**) and 177.5(1)° (**10**). Like the free isoquinoline-phosphine **1** both arsine complexes **9** and **10** are associated to dimers *via* $\pi$-stacking interactions of the (iso)quinoline groups.

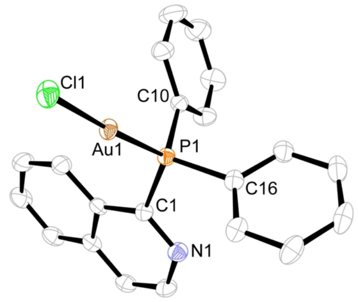


Fig. 5. Molecular structure of **7**. Selected bond lengths (Å) and angles (deg): Au1–P1 2.239(1), Au1–Cl1 2.296(1), P1–C1 1.854(3), P1–C10 1.814(3), P1–C16 1.818(2); Cl1–Au1–P1 175.2(1), Au1–P1–C1 118.7(1), C1–P1–C10 103.3(1).

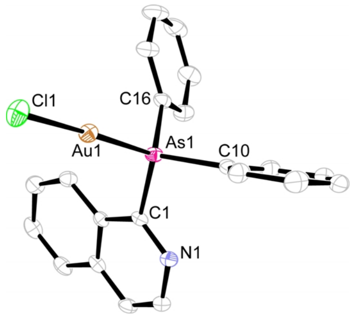


Fig. 6. Molecular structure of **10**. Selected bond lengths (Å) and angles (deg): Au1–As1 2.345(1), Au1–Cl1 2.291(1), As1–C1 1.966(3), As1–C10 1.942(4), As1–C16 1.939(4); As1–Au1–Cl1 177.5(1), Au1–As1–C1 115.3(1), C1–As1–C10 103.2(2).

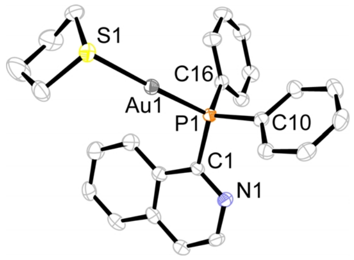
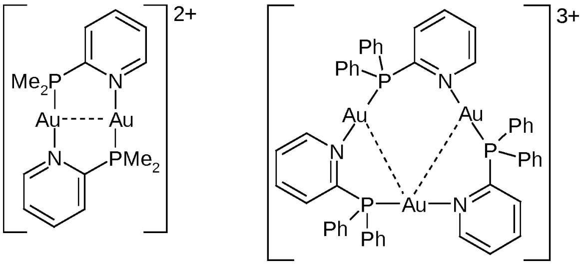


Fig. 7. Complex cation in crystals of **14**. Selected bond lengths (Å) and angles (deg): Au1–S1 2.343(1), Au1–P1 2.278(1), P1–C1 1.840(5), P1–C10 1.822(5), P1–C16 1.815(5); S1–Au1–P1 174.4(1), Au1–P1–C1 111.6(2), C1–P1–C10 108.0(2).

Crystals of **14** are triclinic, space group $P\bar{1}$, with 2 formula units in the unit cell. The coordination of the gold atom is linear [P–Au–S 174.4(1)°] with standard Au–S and Au–P bond lengths [8]. The tetrahydrothiophene ring has a distorted envelope conformation with the sulfur atom in a steep pyramidal configuration (Fig. 7). The situation resembles that of the [(Me$_2$S)(PPh$_3$)Au]$^+$ cation in its tetrafluoroborate salt [37]. Again, $\pi$-stacking interactions of the iso-



Scheme 3. Dinuclear *vs*. trinuclear assembly of $[(P\cap N)Au]^+$ cations.

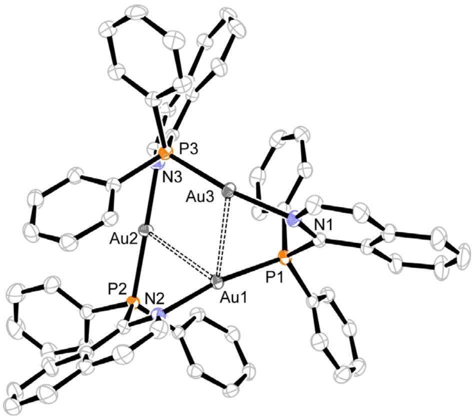


Fig. 8. Trinuclear cation in the crystals of **11**.

quinoline moieties but no short Au ··· Au contacts are present.

Single crystals of **11** and **12** were obtained by slow gas-phase diffusion of diethyl ether into an acetonitrile solution; single crystals of **13** are obtained from acetonitrile/dichloromethane. Compound **11** crystallizes with three molecules of acetonitrile per formula unit in the monoclinic space group $P2_1/c$ with $Z = 4$. Crystals of **12** are monoclinic, space group $C2/c$, with 8 formula units in the unit cell. Compound **13** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 8$. The asymmetric unit consists of two trinuclear aggregates. There are no solvent molecules in the lattice of **12** and one molecule of acetonitrile per trinuclear aggregate in crystals of **13**.

Table 2. Selected bond lengths (Å) and angles (deg) in the trinuclear cations in **11** – **13**.

| | **11** | **12** | **13a** | **13b** |
|---|---|---|---|---|
| Au1 ··· Au2 | 3.164(1) | 3.200(1) | 3.168(1) | 3.192(1) |
| Au1 ··· Au3 | 3.017(1) | 3.059(1) | 3.031(1) | 3.138(1) |
| Au2 ··· Au3 | 4.108(1) | 4.033(1) | 3.854(1) | 3.862(1) |
| Au1–P1 | 2.256(1) | 2.239(2) | 2.241(2) | 2.238(2) |
| Au2–P2 | 2.253(1) | 2.242(2) | 2.243(2) | 2.242(2) |
| Au3–P3 | 2.244(1) | 2.232(2) | 2.243(2) | 2.237(2) |
| Au1–N2 | 2.108(3) | 2.103(5) | 2.077(6) | 2.088(6) |
| Au2–N3 | 2.110(3) | 2.085(6) | 2.097(6) | 2.093(6) |
| Au3–N1 | 2.113(3) | 2.096(6) | 2.104(6) | 2.097(6) |
| P1–Au1–N2 | 170.1(1) | 170.4(2) | 172.3(2) | 170.0(2) |
| P2–Au2–N3 | 171.5(1) | 175.1(2) | 174.0(2) | 171.1(2) |
| P3–Au3–N1 | 172.4(1) | 170.2(2) | 168.4(2) | 171.6(2) |

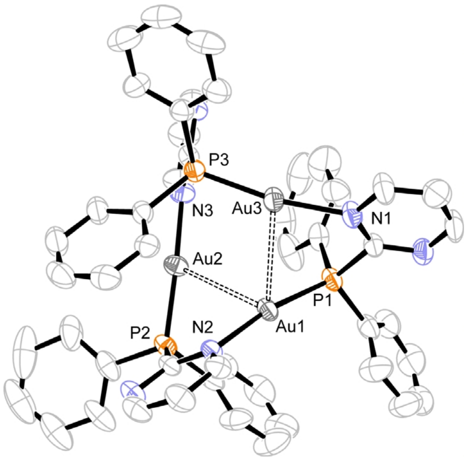


Fig. 9. Trinuclear cation in the crystals of **12** (ORTEP; displacement ellipsoids at the 30 % probability level).

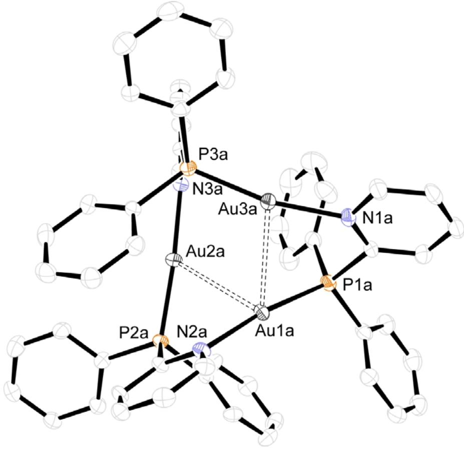


Fig. 10. Trinuclear cation in the crystals of **13** containing the gold atoms Au1a–Au3a.

With the P∩N ligands $Me_2Ppy$ and $Ph_2Pim$, the dinuclear complex cations $[(P\cap N)_2Au_2]^{2+}$ with a head-to-tail configuration of the P∩N ligands are formed [8, 12]. Surprisingly, with the very similar phosphine ligands $Ph_2Ppy$, **2**, and **3** the fragments aggregate to cyclic trinuclear cations forming a twelve-membered ring (Scheme 3, Figs. 8 – 10, Table 2). The structural characteristics of these rings in compound **11** – **13** are very similar: The phosphines act as bridges connecting the gold atoms, which are bound

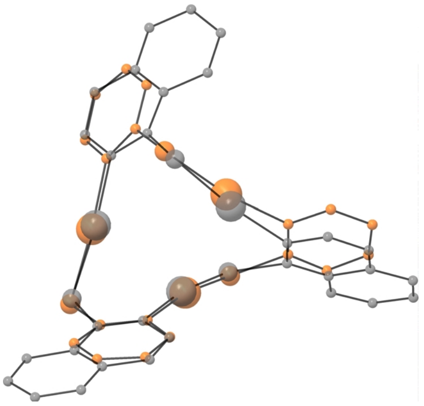


Fig. 11. Superposition of the twelve-membered rings in the crystals of **11** and **12**.

to the phosphorus and the nitrogen atoms in a cyclic (P–Au–N)$_3$ arrangement. The three gold atoms are associated *via* two pairs of short aurophilic interactions connecting the atoms Au1–Au2 and A1–Au3, thus stabilizing the ring structure. The distances of the third pair (Au2–Au3) are out of the standard range for Au$\cdots$Au bonds. Due to the attractive gold-gold interactions the P–Au–N units deviate from linearity. Accordingly, the angle P1–Au1–N2 is the smallest because Au1 binds to both Au2 and Au3 (Table 2). All Au–P distances are comparable to the ones observed for the other phosphine gold complexes presented in this paper, and the Au–N distances are similar to the bond length found in $[(Me_2Ppy)_2Au_2]^{2+}$ [Au–N 2.09(2) Å] [8]. The large conformational similarities between the cyclic aggregates are illustrated in Fig. 11, depicting a superposition of the core ring structures of **11** and **12**.

Taking into account that all up to now reported [(P∩N)Au]An complexes (An = weakly or non-coordinating anion) crystallize as dimers, it cannot be ruled out that beside the presented trinuclear compounds other polymorphs of **11** – **13** consisting of dinuclear units exist. These polymorphs might be isolated under different conditions (temperature, solvent, concentration) [38]. Polymorphism of gold(I) complexes is well known from the literature: *e. g.*, the complex $(Me_2PhP)AuCl$ crystallizes as dimer or trimer, the latter not unlike to the trinuclear structure described above [39].

### *Photophysical studies*

The photophysical properties of dinuclear and polynuclear gold(I) complexes have been thoroughly investigated [40 – 42]. In the solid state complexes with Au$\cdots$Au contacts exhibit long-lived emissions in the visible region upon photoexcitation. The origins of the emissions are as multifarious as the aggregation patterns of these complexes but are usually attributed to excited states involving aurophilic interactions: These Au$\cdots$Au interactions lower the energy of the $5d\sigma^* \rightarrow 6p\sigma$ transition ($5d\sigma^*$ and $6p\sigma$ refer to the antibonding combination of the $5d_{z^2}$ and to the bonding combination of the $6s/6p_z$ orbitals, respectively; the Au$\cdots$Au axis is defined as $z$ axis), and the emissions are assigned to the $^3[d\sigma^* p\sigma]$ excited state, which has a formal metal-metal bond. This interpretation was confirmed by Omary and co-workers, who investigated the luminescence of RNC–Au–Cl complexes in the solid state. The covalent Au–Au bonding in the excited state and the weak aurophilic Au$\cdots$Au contact in the ground state explain the large excited-state distortion [4]. This means that the emissive state is an Au–Au bonded excited state formed upon photoexcitation, similar to organic excimers. Therefore, in solution photo-luminescence is only observable if the aurophilic interactions are retained, *e. g.* by employing bidentate ligands. The prototypical example of such complexes is $[Au_2(R_2PCH_2PR_2)_2]^{2+}$ (R = alkyl, aryl), which preserves its dinuclear structure also in solution. Che *et al.* suggested an exciplex formation with either a solvent molecule or a counter ion as the reason for the phosphorescence in the visible region. This argumentation resembles the situation in three-coordinate Au(I) complexes [43 – 45].

Due to the short aurophilic interactions in the crystals of **11** – **13** we anticipated emissive behavior. Indeed, UV/Vis excitation at room temperature of solvent-free crystals causes red-orange emissions (Fig. 12). The broad emission bands have maxima at 552, 580 and 613 nm for complex **11**, at 628 and 460 nm (shoulder) for complex **12**, and at 617 and 524 nm for complex **13**. The shape of the excitation bands of the three complexes is very similar, consisting of maxima at 349, 350 and 388 nm and high-energy shoulders at 291, 302, 341 nm for **13**, **12**, and **11**, respectively. The large energy shifts of $\approx 7700$ cm$^{-1}$ (**11**) and $\approx 12600$ cm$^{-1}$ (**12** and **13**) indicate severe distortions of the structures in the excited state, and the similarities in the electronic spectra of **12** (R = pym) and **13** (R = py) indicate that not only the solid-state structures are very similar but also the electronic structure. Because of the absence

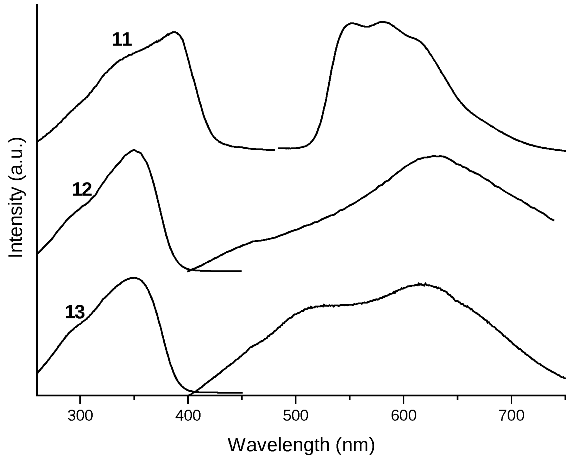


Fig. 12. Excitation (left) and emission (right) spectra of crystals of **11**–**13** at 20 °C (emission spectra: **11** $\lambda_{ex}$ = 400 nm, **12**, **13** $\lambda_{ex}$ = 380 nm; excitation spectra: $\lambda_{det}$ = 600 nm).

of coordinating anions or solvent molecules we favor a luminescence mechanism *via* an Au–Au bond from the excited state of $^3[d\sigma^* p\sigma]$-character. The low affinity of the nitrogen donor functions towards gold(I) atoms makes the conservation of the trinuclear aggregate dissolved in polar and/or coordinating solvents unlikely. As the emissions are based on aurophilic interactions which are only present in the solid state and not in solution, it is not surprising that this emission is lost in acetonitrile solution at ambient temperature. Due to the insolubility of the complexes **11**–**13** in unpolar solvents, no further investigations were performed.

## Conclusion

We have shown that marginal variations of the ligand structures strongly effect the aggregation pattern of the resulting gold(I) complexes in the solid state. The ligands E∩N (E = P, As) form chloro-gold(I) complexes with standard rod-like structures without aggregation *via* aurophilc interactions. However, upon treatment of these complexes with $AgBF_4$ unprecedented trinuclear aggregates were obtained. Despite the fact that in the absence of coordinating anions the majority of the reported (P∩N)-gold(I) complexes form dinuclear cations, complexes **11**–**13** oligomerize to trinuclear units building twelve-membered rings stabilized by two pairs of short aurophilic interactions. Due to the presence of Au···Au interactions, the complexes are luminescent in the solid state, but not in acetonitrile solution.

## Experimental Section

### General information

All commercially available solvents and starting materials were used without further purification. The grade of gaseous $NH_3$ was 5.0. (tht)AuCl [46] and $[(Ph_2Ppy)_2Au_2] \cdot 2BF_4$ [8] were prepared according to described procedures. Elemental analyses were carried out by the Center for Chemical Analysis of the Faculty of Natural Sciences of the Universität Regensburg. Emission/Excitation spectra were recorded on a Jobin Yvon Horiba 'Fluorolog-3' fluorescence spectrophotometer using quartz plates. NMR spectra were obtained on a Bruker Avance 300 instrument ($T$ = 300 K). Chemical shifts are reported in $\delta$ (ppm) relative to external standards (solvent residual peak, 85 % $H_3PO_4$). The spectra were analyzed by first order. Characterization of the signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad singlet, dd = double doublet, dt = double triplet, ddd = double double doublet. Mass spectra were recorded on a Varian CH-5 (EI) and a Finnigan MAT TSQ 7000 (ESI) instrument.

### Crystal structure determination

Single-crystal X-ray data were collected on two different diffractometer systems. For compounds **3**, **12** and **13**, a Nonius Kappa diffractometer with a CCD area detector was employed, using the program suite COLLECT [47, 48]. Data collections for crystals of the compounds **2**, **6**, **7**, **9**–**11**, and **14** were performed on a Stoe-IPDS diffractometer [49]. On both diffractometers graphite-monochromatized Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) was used. The crystal structures were determined by Direct Methods and subsequent Fourier and difference Fourier syntheses (SHELXS [50] and SIR-97 [51]), followed by full-matrix least-squares refinement on $F^2$ (SHELXL-97) [52].

The hydrogen atoms were calculated geometrically, and a riding model was applied during the refinement process, except for compound **3**, where all hydrogen atoms could be located from the difference Fourier maps and were refined freely. All non-hydrogen atoms were refined anisotropically except for the boron and fluorine atoms in **12** which were refined isotropically. The $BF_4$ groups in compounds **12** and **13** showed strong disorder even at 120 K. The $B(4)F_4$ anion in **12** is disordered about the center of inversion at $^1/_4$ $^1/_4$ 0.

The location of the $BF_4$ anions of **13** from the difference Fourier maps was only partially successful, since only five out of six $BF_4$ anions could be located and refined using restraints. The sixth anion, however, remains elusive. It seems to be located within the cavities between the molecules, as also suggested by the substantial residual electron density. Crystal data and details of the measurement and refinement are given in Tables 3 and 4.

Supplementary crystallographic data for this paper have been deposited. These data can be obtained free of charge *via*

Table 3. Crystal data, data collection and structure refinement for compounds **2**, **3, 6**, **7**, **9**, and **10**.

| | **2** | **3** | **6** | **7** | **9** | **10** |
|---|---|---|---|---|---|---|
| Formula | $C_{21}H_{16}NP$ | $C_{16}H_{13}N_2P$ | $C_{21}H_{16}AuClNP$ | $C_{21}H_{16}AuClNP$ | $C_{21}H_{16}AsAuClN$, $0.5(C_4H_{10}O)$ | $C_{21}H_{16}AsAuClN$, $0.5(C_4H_{10}O)$ |
| $M_r$ | 313.32 | 264.25 | 545.74 | 545.74 | 626.74 | 626.74 |
| Crystal size, mm$^3$ | 0.42×0.40×0.36 | 0.32×0.18×0.12 | 0.35×0.26×0.17 | 0.51×0.25×0.08 | 0.38×0.24×0.14 | 0.25×0.21×0.17 |
| Crystal system | triclinic | monoclinic | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P\bar{1}$ | $C2/c$ | $P2_1/n$ | $P2_1/c$ |
| $a$, Å | 8.447(1) | 8.995(1) | 9.768(1) | 17.710(1) | 7.3983(7) | 15.179(1) |
| $b$, Å | 8.990(1) | 10.078(1) | 10.601(1) | 7.799(1) | 11.4332(8) | 9.1344(4) |
| $c$, Å | 11.823(1) | 17.129(2) | 11.032(1) | 28.345(2) | 25.393(3) | 16.135(1) |
| $\alpha$, deg | 84.41(1) | 90 | 115.53(1) | 90 | 90 | 90 |
| $\beta$, deg | 78.72(1) | 115.90(2) | 90.93(1) | 101.85(1) | 97.82(1) | 105.27(1) |
| $\gamma$, deg | 65.34(1) | 90 | 110.48(1) | 90 | 90 | 90 |
| $V$, Å$^3$ | 800.0(2) | 1396.8(3) | 946.7(3) | 3831.9(5) | 2127.9(4) | 2158.2(3) |
| $\rho_{calc}$, g cm$^{-3}$ | 1.30 | 1.26 | 1.91 | 1.89 | 1.96 | 1.93 |
| $Z$ | 2 | 4 | 2 | 8 | 4 | 4 |
| $\mu$, mm$^{-1}$ | 0.2 | 0.2 | 8.0 | 7.9 | 8.6 | 8.5 |
| $T$, K | 123 | 273 | 123 | 123 | 123 | 123 |
| $\Theta$ range, deg | 2.49 – 26.82 | 4.18 – 24.70 | 2.76 – 26.82 | 2.50 – 26.89 | 2.41 – 26.91 | 2.77 – 26.92 |
| Reflections collected | 12296 | 4305 | 14767 | 21689 | 22093 | 21209 |
| Unique reflections / $R_{int}$ | 3137 / 0.0365 | 2355 / 0.0323 | 3774 / 0.0690 | 4101 / 0.0365 | 4577 / 0.0270 | 4631 / 0.0534 |
| Observed refl. $[I \geq 2\sigma(I)]$ | 2954 | 1863 | 3673 | 3631 | 4028 | 4346 |
| Param. refined | 208 | 225 | 201 | 226 | 242 | 245 |
| Absorption correction | none | multi-scan | analytical from crystal shape | numerical numerical | analytical from crystal shape | analytical from crystal shape |
| $T_{min}/T_{max}$ | – | 0.9945 / 0.9982 | 0.1378 / 0.3585 | 0.1079 / 0.5501 | 0.1738 / 0.3476 | 0.1710 / 0.3474 |
| $R1[I \geq 2\sigma(I)]/wR2$ | 0.0349 / 0.0913 | 0.0535 / 0.1766 | 0.0289 / 0.0766 | 0.0197 / 0.0540 | 0.0228 / 0.0583 | 0.0283 / 0.0734 |
| $\Delta\rho_{fin}$ (max/min), e Å$^{-3}$ | 0.423 / −0.202 | 0.48 / −0.21 | 2.851 / −0.825 | 0.485 / −0.984 | 1.592 / −0.586 | 1.949 / −0.609 |
| CCDC number | 719337 | 719338 | 719339 | 719340 | 719341 | 719342 |

www.ccdc.cam.ac.uk/data_request/cif. The respective CCDC numbers are listed in Tables 3 and 4.

### *8-(Diphenylphosphino)quinoline (Ph$_2$Pqn), **1***

The phosphine ligand **1** was synthesized following a literature procedure [15]. Complementary analytical data: $M_r$ = 313.10. – $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.87 (dd, $^3J_{HH}$ = 4.3 Hz, $^4J_{HH}$ = 1.7 Hz, C2-H, 1 H), 8.16 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.7 Hz, C4-H, 1 H), 7.36 – 7.47 (m, C5/C6-H, 2 H), 7.39 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.3 Hz, C3-H, 1 H), 7.27 – 7.34 (m, Ph-H, 10 H), 7.12 (ddd, $^3J_{PH}$ = 7.1 Hz, $^3J_{HH}$ = 3.8 Hz, $^4J_{HH}$ = 1.4 Hz, C7-H). – $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 148.73 (d, $^4J_{CP}$ = 1.5 Hz, C2), 148.51 (d, $^2J_{CP}$ = 17.0 Hz, C8a), 137.37 (d, $J_{CP}$ = 11.8 Hz), 136.39 (d, $J_{CP}$ = 11.1 Hz), 135.09 (d, $J_{CP}$ = 2.2 Hz), 133.10 (d, $^2J_{CP}$ = 19.9 Hz, C2′), 131.20 (d, $J_{CP}$ =10.3 Hz), 127.71 (s), 127.45 (s), 127.30 (d, $J_{CP}$ = 6.6 Hz, C3′), 126.40 (s), 125.47 (s), 120.31 (s, C3). – $^{31}$P NMR (121.45 MHz, $CDCl_3$): $\delta$ = −14.34 ppm. – MS (EI, 70 eV): $m/z$ (%) = 313.1 (100) $[M]^+$, 312.1 (89) $[M–H]^+$, 236.1 (47) $[M–Ph]^+$, 235.1 (57) $[M–PhH]^+$, 204.0 (41) $[M–PhPH]^+$, 183.0 (18) $[Ph_2P]^+$, 159.0 (11) $[qnP]^+$, 117.6 (50) $[M–PhH]^{2+}$.

### *1-(Diphenylphosphino)isoquinoline (Ph$_2$Piqn), **2***

The phosphine ligand **2** was prepared as described for **1**. Yield: 74 %, m. p. 145 – 147 °C. – $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.63 (ddd, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 4.4, $^4J_{HH}$ = 0.8 Hz, 1 H, C8-H), 8.59 (d, $^3J_{HH}$ = 5.8 Hz, 1 H, C3-H), 7.82 (d, $J_{HH}$ = 8.0 Hz, 1 H, C5-H), 7.65 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.1 Hz, 1 H, C6-H), 7.58 (d, $^3J_{HH}$ = 5.8 Hz, 1 H, C4-H), 7.52 (ddd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.9 Hz, 1 H, C7-H), 7.38 – 7.45 (AA′BB′C, C2′/C6′-H, 4 H), 7.30 – 7.36 (AA′BB′C, C3′/C5′-H, 4 H). – $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 162.62 (d, $^1J_{CP}$ = 9.6 Hz, C1), 142.21 (d, $^3J_{CP}$ = 3.7 Hz, C3), 134.87 (d, $J_{CP}$ = 7.4 Hz), 134.29 (d, $J_{CP}$ = 4.4 Hz), 133.44 (d, $^2J_{CP}$ = 19.9 Hz, C2′), 130.98 (d, $^1J_{CP}$ = 29.5 Hz), 128.95 (s), 127.83 (s), 127.32 (d, $J_{CP}$ = 7.4 Hz, C3′), 126.27 (d, $J_{CP}$ = 2.2 Hz), 126.09 (d, $^1J_{CP}$ = 1.5 Hz), 125.82 (d, $^1J_{CP}$ = 23.6 Hz), 119.34 (s, C4). – $^{31}$P NMR (121.45 MHz, $CDCl_3$): $\delta$ = −7.60 ppm. – MS (EI, 70 eV): $m/z$ (%) = 313.1 (67) $[M]^+$, 312.1 (100) $[M–H]^+$, 235.1 (42) $[M–C_6H_6]^+$, 183.0 (27) $[M–iqn–2H]^+$. – $C_{21}H_{16}NP$ (313.10): calcd. C 80.50, H 5.15, N 4.47; found C 80.30, H 5.20, N 4.42.

### *2-(Diphenylphosphino)pyrimidine (Ph$_2$Ppym), **3***

The phosphine ligand **3** was prepared as described for **1**. Complementary analytical data: Yield: 76 %, m. p. 118 – 119 °C. – $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.70 (d, $^3J_{HH}$ = 4.9 Hz, 2 H, C4/6-H), 7.47 – 7.58 (m, 4 H, Ph-H), 7.33 – 7.41 (m, 6 H, Ph-H), 7.12 (dt, $^3J_{HH}$ = 4.9, $^5J_{HP}$ = 1.1 Hz, 1 H, C5-H). – $^{13}$C NMR (75.5 MHz, $CDCl_3$):

Table 4. Crystal data, data collection and structure refinement for compounds **11** – **14**.

| | **11** | **12** | **13** | **14** |
|---|---|---|---|---|
| Formula | $C_{63}H_{48}Au_3N_3P_3$, 3($C_2H_3N$), 3($BF_4$) | $C_{48}H_{39}Au_3N_6P_3$, 3($BF_4$) | $C_{51}H_{42}Au_3N_3P_3$, $C_2H_3N$, 3($BF_4$) | $C_{25}H_{24}AuNPS$, $BF_4$ |
| $M_r$ | 1914.46 | 1644.09 | 1682.17 | 685.27 |
| Crystal size, mm$^3$ | 0.25 × 0.20 × 0.14 | 0.80 × 0.45 × 0.40 | 0.32 × 0.30 × 0.20 | 0.31 × 0.27 × 0.18 |
| Crystal system | monoclinic | monoclinic | monoclinic | triclinic |
| Space group | $P2_1/c$ | $C2/c$ | $P2_1/c$ | $P\bar{1}$ |
| $a$, Å | 13.971(1) | 43.733(1) | 23.5452(5) | 10.124(1) |
| $b$, Å | 25.047(2) | 12.5915(2) | 21.7183(4) | 10.243(1) |
| $c$, Å | 19.777(1) | 22.0117(3) | 24.2355(5) | 13.501(2) |
| $\alpha$, deg | 90 | 90 | 90 | 68.81(1) |
| $\beta$, deg | 101.207(8) | 113.097(1) | 105.873(1) | 71.69(1) |
| $\gamma$, deg | 90 | 90 | 90 | 81.50(2) |
| $V$, Å$^3$ | 6788.4(8) | 11149.3(3) | 11920.6(4) | 1238.2(3) |
| $\rho_{calc}$, g cm$^{-3}$ | 1.87 | 1.96 | 1.87 | 1.84 |
| $Z$ | 4 | 8 | 8 | 2 |
| $\mu$, mm$^{-1}$ | 6.6 | 8.0 | 7.5 | 6.1 |
| $T$, K | 123 | 293 | 120 | 123 |
| $\Theta$ range, deg | 1.83 – 25.83 | 4.13 – 28.27 | 4.11 – 30.51 | 2.23 – 25.74 |
| Reflections collected | 61619 | 26750 | 71134 | 12977 |
| Unique reflections / $R_{int}$ | 12985 / 0.0379 | 13748 / 0.0229 | 36208 / 0.0270 | 4395 / 0.0635 |
| Observed refl. [$I \geq 2\sigma(I)$] | 11302 | 10537 | 29418 | 4395 |
| Param. refined / restraints | 868 / 0 | 781 / 0 | 1216 / 5 | 307 / 0 |
| Absorption correction | analytical from crystal shape | multi-scan | multi-scan | analytical from crystal shape |
| $T_{min}/T_{max}$ | 0.2515 / 0.4882 | 0.5655 / 0.7392 | 0.8060 / 0.8642 | 0.1797 / 0.3815 |
| $R1[I \geq 2\sigma(I)]/wR2$ | 0.0231 / 0.0572 | 0.0516 / 0.1304 | 0.0481 / 0.1526 | 0.0308 / 0.0784 |
| $\Delta\rho_{fin}$ (max/min), e Å$^{-3}$ | 1.801 / −0.615 | 1.21 / −1.20 | 6.80 / −1.34 | 1.592 / −0.586 |
| CCDC number | 719343 | 719344 | 719345 | 719346 |

$\delta$ = 155.98 (d, $^3J_{CP}$ = 6.0 Hz, C4/6), 134.93 (d, $^1J_{CP}$ = 7.6 Hz, C1′), 134.08 (d, $^2J_{CP}$ = 20.1 Hz, C2′/6′), 128.72 (s, C4′), 127.94 (d, $^3J_{CP}$ = 7.8 Hz, C3′/5′), 118.28 (s, C5), quaternary C2 not detected. – $^{31}$P NMR (121.45 MHz, $CDCl_3$): $\delta$ = 1.32 ppm. – (EI-MS, 70 eV): $m/z$ (%) = 264.3 (100) [M]$^+$, 187.2 (26) [M–$C_6H_5$]$^+$. – $C_{16}H_{13}N_2P$ (264.27): calcd. C 72.72, H 4.96, N 10.60; found C 72.60, H 5.02, N 10.63.

### *8-(Diphenylarsino)quinoline (Ph$_2$Asqn),* ***4***

The arsine ligand **4** was synthesized following a literature procedure [15]. Complementary analytical data: $M_r$ = 357.28. – $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.88 (dd, $^3J_{HH}$ = 4.3 Hz, $^4J_{HH}$ = 1.7 Hz, C2-H, 1 H), 8.17 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.7 Hz, C4-H, 1 H), 7.82 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, C5-H, 1 H), 7.43 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.9 Hz, C6-H, 1 H), 7.40 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.3 Hz, C3-H, 1 H), 7.30 – 7.35 (m, Ph-H, 10 H), 7.27 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.4 Hz, C7-H). – $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 150.13 (C8a), 149.92 (C2), 141.78, 139.99, 136.25, 134.69, 134.16 (C2′), 128.67, 128.57, 128.28 (C3′), 128.09, 126.83, 121.40 (C3). – MS (EI, 70 eV): $m/z$ (%) = 357.1 (69) [M]$^+$, 356.1 (21) [M–H]$^+$, 280.1 (56) [M–Ph]$^+$, 279.1 (57) [M–PhH]$^+$, 204.1 (100) [M–PhAsH]$^+$, 152.0 (37) [PhAs]$^+$, 139.6 (28) [M–PhH]$^{2+}$.

### *1-(Diphenylarsino)isoquinoline (Ph$_2$Asiqn),* ***5***

The arsine ligand **5** was prepared as described for **4**. Yield: 80.9 %, m. p. 126 – 128 °C. – $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.61 (d, $^3J_{HH}$ = 5.8 Hz, 1 H, C3-H), 8.55 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, C8-H), 7.83 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, C5-H), 7.67 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, C6-H), 7.59 (d, $^3J_{HH}$ = 5.8 Hz, 1 H, C4-H), 7.55 (ddd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, C7-H), 7.47 – 7.52 (AA′BB′C, C2′/C6′-H, 4 H), 7.31 – 7.37 (AA′BB′C, C3′/C5′-H, 4 H). – $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 166.87 (C1), 142.32 (C3), 138.09, 134.30, 133.21 (C2′), 131.56, 128.94, 128.15, 127.46 (C3′), 126.44, 126.34, 126.11, 119.21. – $C_{21}H_{16}NAs$ (357.29): calcd. C 70.60, H 4.51, N 3.92; found C 70.46, H 4.63, N 3.63.

### *Synthesis of chloro(phosphine/arsine)gold(I) complexes*

### *General procedure*

All L–Au–Cl (L = ligands **1** – **5**) complexes were prepared following a published procedure [32]: Equimolar amounts of (tht)AuCl and the phoshine/arsine ligand were stirred at r. t. in $CH_2Cl_2$. The products were precipitated with *n*-pentane. Filtration gave compounds **6** – **10** in high yields.

### *[8-(Diphenylphosphino)quinoline]gold(I) chloride,* ***6***

Yield: 96 %. – $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.79 (dd, $^{3}J_{HH}$ = 4.3 Hz, $^{4}J_{HH}$ = 1.6 Hz, C2-H, 1H), 8.51 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 1.6 Hz, C3-H, 1H), 8.24 (d, $^{3}J_{HH}$ = 8.2 Hz, C3-H, 1H), 7.46 – 7.62 (m, 7 H), 7.37 – 7.46 (m, 5 H), 7.22 (ddd, $^{3}J_{PH}$ = 12.9 Hz, $^{3}J_{HH}$ = 7.1 Hz, $^{4}J_{HH}$ = 1.4 Hz, C7-H, 1H). – $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 150.27 (C8a), 147.77 (d, $^{4}J_{CP}$ = 7.4 Hz, C2), 136.19, 135.66 (d, $J_{CP}$ = 6.6 Hz), 134.40 (d, $J_{CP}$ = 14.7 Hz, C2′), 132.47 (d, $J_{CP}$ = 3.0 Hz), 131.56 (d, $J_{CP}$ = 3.0 Hz), 129.77, 129.02 (d, $J_{CP}$ = 12.5 Hz, C3′), 128.34 (d, $J_{CP}$ = 5.9 Hz), 127.99, 126.07, 122.38 (C3). – $^{31}$P NMR (121.45 MHz, CDCl$_3$): $\delta$ = 26.89 ppm. – MS (ESI, CH$_2$Cl$_2$/MeCN): $m/z$ (%) = 1055.2 (6) [(LAu)$_2$Cl]$^+$, 823.3 (100) [L$_2$Au]$^+$, 551.1 (3) [LAu+MeCN]$^+$. – C$_{21}$H$_{16}$NPAuCl · 2CH$_2$Cl$_2$ (545.75): calcd. C 38.60, H 2.82, N 1.96; found C 38.16, H 2.73, N 1.92.

### *[1-(Diphenylphosphino)isoquinoline]gold(I) chloride,* ***7***

Yield: 96 %. – $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.61 (d, $J_{HH}$ = 8.5 Hz, 1 H), 8.56 (dd, $J_{HH}$ = 5.5, 1.1 Hz, 1 H), 7.92 (d, $J_{HH}$ = 8.2 Hz, 1 H), 7.79 (dd, $J_{HH}$ = 5.77, 2.47 Hz, 1 H), 7.71 (ddd, $J_{HH}$ = 8.24, 7.14, 1.10 Hz, 1 H), 7.43 – 7.67 (m, 11 H). – $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 152.87 (d, $J_{CP}$ = 82.6 Hz), 136.14 (d, $J_{CP}$ = 5.9 Hz), 135.10 (d, $J_{CP}$ = 14.0 Hz), 132.13 (d, $J_{CP}$ = 2.2 Hz), 130.89, 129.99 (d, $J_{CP}$ = 25.1 Hz), 129.12 (d, $J_{CP}$ = 11.8 Hz), 128.62, 128.31, 128.03 (d, $J_{CP}$ = 2.2 Hz), 127.43, 125.81 (d, $J_{CP}$ = 8.9 Hz), 123.45 (d, $J_{CP}$ = 2.9 Hz). – $^{31}$P NMR (121.45 MHz, CDCl$_3$): $\delta$ = 28.8 ppm. – MS (ESI, CH$_2$Cl$_2$/MeCN): $m/z$ (%) = 1055.2 (12) [(LAu)$_2$Cl]$^+$, 823.3 (100) [L$_2$Au]$^+$, 551.1 (11) [LAu+MeCN]$^+$, 314.1 [LH]$^+$. – C$_{21}$H$_{16}$NPAuCl (545.76): calcd. C 46.22, H 2.95, N 2.57; found C 46.05, H 3.01, N 2.43.

### *[2-(Diphenylphosphino)pyrimidine]gold(I) chloride,* ***8***

Yield: 93 %. – $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.84 (d, $^{3}J_{HH}$ = 4.9 Hz, 2 H, C4/6-H), 7.69 – 7.81 (m, 4 H, Ph-H), 7.43 – 7.58 (m, 6 H, Ph-H), 7.36 (dt, $^{3}J_{HH}$ = $^{5}J_{HP}$ = 4.6 Hz, 1 H, C5-H). – $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 156.98 (d, $^{3}J_{CP}$ = 13.0 Hz, C4/6), 134.31 (d, $^{2}J_{CP}$ = 14.0 Hz, C2′/6′), 131.70 (s, C4′), 128.54 (d, $^{3}J_{CP}$ = 12.2 Hz, C3′/5′), 127.04 (d, $^{1}J_{CP}$ = 62.9 Hz, C1′), 120.95 (s, C5), quaternary C2 not detected. – $^{31}$P NMR (121.45 MHz, CDCl$_3$): $\delta$ = 35.00 ppm. – MS (ESI, CH$_2$Cl$_2$/MeOH): $m/z$ (%) = 957.1 (100) [(LAu)$_2$Cl]$^+$, 725.1 (67) [L$_2$Au]$^+$, 513.9 (26) [LAuCl+NH$_4$]$^+$, 477.9 (68) [LAu+O]$^+$. – C$_{16}$H$_{13}$N$_2$PAuCl (496.69): calcd. C 38.69, H 2.64, N 5.64; found C 38.67, H 2.59, N 5.63.

### *[8-(Diphenylarsino)quinoline]gold(I) chloride,* ***9***

Yield: 98 %. – $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.79 (dd, $^{3}J_{HH}$ = 4.1 Hz, $^{4}J_{HH}$ = 1.7 Hz, C2-H, 1 H), 8.22 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 1.7 Hz, C4-H, 1 H), 8.02 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 1.4 Hz, C5-H, 1 H), 7.38 – 7.58 (m, 13 H). – $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 150.55 (C8a), 147.97 (C2), 136.19, 134.80, 133.51 (C2′), 131.83, 131.80, 131.77, 131.03, 129.34 (C3′), 128.65, 126.41, 122.41 (C3). – MS (ESI, CH$_2$Cl$_2$/MeCN): $m/z$ (%) = 1143.1 (1) [(LAu)$_2$Cl]$^+$, 911.1 (100) [L$_2$Au]$^+$, 595.0 (1) [LAu+MeCN]$^+$, 554.0 (0.5) [LAu]$^+$, 358.1 (3.5) [LH]$^+$. – C$_{21}$H$_{16}$NAsAuCl (589.71): calcd. C 42.77, H 2.73, N 2.38; found C 42.61, H 2.59, N 2.31.

### *[1-(Diphenylarsino)isoquinoline]gold(I) chloride,* ***10***

Yield: 94 %. – $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.60 (d, $J_{HH}$ = 8.5 Hz, 1 H), 8.55 (d, $J_{HH}$ = 5.5 Hz, 1 H), 7.92 (d, $J_{HH}$ = 7.9 Hz, 1 H), 7.78 (d, $J_{HH}$ = 5.8 Hz, 1 H), 7.72 (dd, $J_{HH}$ = 7.6 Hz, 1 H), 7.62 – 7.65 (m, 4 H), 7.42 – 7.55 (m, 10 H). – $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 156.49, 142.79, 136.39, 134.01, 131.04, 130.98, 130.58, 129.49, 128.83, 127.97, 125.96, 125.96, 123.18. – MS (ESI, CH$_2$Cl$_2$/MeCN): $m/z$ (%) = 1143.1 (1) [(LAu)$_2$Cl]$^+$, 911.1 (100) [L$_2$Au]$^+$, 595.0 (3) [LAu+MeCN]$^+$, 358.1 (20) [LH]$^+$. – C$_{21}$H$_{16}$NAsAuCl (589.71): calcd. C 42.77, H 2.73, N 2.38; found C 43.02, H 2.91, N 2.41.

### *[1-(Diphenylphosphino)isoquinoline]gold(I) tetrafluoroborate,* ***11***

To a solution of **7** (100 mg, 0.18 mmol) in acetonitrile (10 mL) AgBF$_4$ (36 mg, 0.18 mmol) dissolved in acetonitrile (10 mL) was added. After 3 h of stirring in the dark AgCl was removed by filtration, and the filtrate was concentrated *in vacuo*. The addition of diethyl ether gave complex **11** as a colorless powder. Yield: 83 %. – $^{1}$H NMR (300 MHz, CD$_3$CN): $\delta$ = 8.76 (d, $J_{HH}$ = 4.4 Hz, 1 H), 8.2 (br, 1 H), 8.16 (d, $J_{HH}$ = 8.5, 1 H), 8.0 (br, 1 H), 7.87 (dd, $J_{HH}$ = 7.7 Hz, 1 H), 7.40 – 7.65 (m, 11 H). – $^{31}$P NMR (121.45 MHz, CD$_3$CN): $\delta$ = 28.45 ppm. – MS (ESI, MeCN): $m/z$ (%) = 823.2 (31) [L$_2$Au]$^+$, 551.1 (100) [LAu+MeCN]$^+$, 510.1 (4) [LAu]$^+$. – [C$_{21}$H$_{16}$NPAu]BF$_4$ (597.11): calcd. C 42.24, H 2.70, N 2.35; found C 42.33, H 2.83, N 2.36.

### *[2-(Diphenylphosphino)pyrimidine]gold(I) tetrafluoroborate,* ***12***

Complex **12** was prepared as described for **11**. Yield: 79 %. – $^{1}$H NMR (300 MHz, CD$_3$CN): $\delta$ = 9.12 (d, $^{3}J_{HH}$ = 5.2 Hz, 2 H, C4/6-H), 7.87 (br, 1 H, C5-H), 7.53 – 7.72 (m, 10 H, Ph-H). – $^{31}$P NMR (121.45 MHz, CD$_3$CN): $\delta$ = 35.60 ppm. – MS (ESI, MeCN): $m/z$ (%) = 725.2 (100) [L$_2$Au]$^+$, 502.1 (99) [LAu+MeCN]$^+$, 461.0 (3) [LAu]$^+$. – [C$_{16}$H$_{13}$N$_2$PAu]BF$_4$ (548.04): calcd. C 35.07, H 2.39, N 5.11; found C 34.97, H 2.47, N 5.16.

### *[2-(Diphenylphosphino)pyridine]gold(I) tetrafluoroborate, **13***

Complex **13** was prepared as described for **11**. See also ref. [8]. Complementary NMR data: – $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ = 9.12 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, C3$_{Py}$-H), 8.18 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, py-H), 8.0 (br, 1H, py-H), 7.31 – 7.63 (m, 10 H, Ph-H), 7.24 (t, $^3J_{HH}$ = 6.4 Hz, 1 H, py-H). – $^{13}$C NMR (75.5 MHz, $CD_3CN$): $\delta$ = 156.73 (d, $J_{CP}$ = 16.2 Hz, Py-C3), 143.65 (s, py-C), 135.59 (d, $J_{CP}$ = 13.3 Hz, Ph-C), 135.14 (s, Ph-C), 133.89 (d, $J_{CP}$ = 15.4 Hz, py-C), 131.24 (d, $J_{CP}$ = 12.3 Hz, Ph-C), 129.91 (s, py-C), quaternary carbon atoms not detected. – $^{31}$P NMR (121.45 MHz, $CD_3CN$): $\delta$ = 35.15 ppm.

### *[1-(Diphenylphosphino)isoquinoline](tetrahydrothiophene)-gold(I) tetrafluoroborate, **14***

To a solution of (tht)AuCl (51.0 mg, 0.16 mmol) in $CH_2Cl_2$ (10 mL) ligand **2** (50.0 mg, 0.16 mmol) was added. After 2 h a suspension of $AgBF_4$ (31.0 mg, 0.16 mmol) in $CH_2Cl_2$ (10 mL) was added. After 3 h of stirring in the dark the AgCl precipitate was removed by filtration, and the filtrate was concentrated *in vacuo*. Addition of diethyl ether yielded complex **14** as a colorless powder. Yield: 67 %. – $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.65 (br, 1 H), 8.3 (br, 1 H), 7.99 (d, $J_{HH}$ = 8.0 Hz, 1 H), 7.92 (d, $J_{HH}$ = 5.5, 1 H), 7.77 (dd, $J_{HH}$ = 8.0 1 H), 7.46 – 7.70 (m, 11 H), 3.50 (t, $^3J_{HH}$ = 6.6 Hz, 4 H, thtC2-H), 2.18 (m, 4 H, thtC3-H). – $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 151.78 (d, $J_{CP}$ = 81.1 Hz), 143.24 (d, $J_{CP}$ = 17.0), 136.46, 134.84 (d, $J_{CP}$ = 13.3), 131.68, 132.93, 130.36 (d, $J_{CP}$ = 21.4), 129.84 (d, $J_{CP}$ = 11.8), 129.04 (d, $J_{CP}$ = 75.2), 126.22, 125.39, 125.04 (d, $J_{CP}$ = 7.4), 124.59, 39.41, 31.04. – $^{31}$P NMR (121.45 MHz, $CDCl_3$): $\delta$ = 32.17 ppm. – $[C_{21}H_{16}NPAuSC_4H_8]BF_4$ (685.28).

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