Gold(I) and silver(I) complexes containing a tripodal tetraphosphine ligand: influence of the halogen and stoichiometry on the properties. The X-ray crystal structure of two gold(I) dimeric aggregates†

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Complexes of the type $[Au_2(\mu\text{-}PP_3)_2]X_2$ [X = Cl (**1**), Br (**2**), I (**3**)], $[Ag_2(\mu\text{-}PP_3)_2](NO_3)_2$ (**4**), $Ag(PP_3)Cl$ (**5**), $M_3(\mu\text{-}PP_3)X_3$ [M = Au, X = Cl (**10**), Br (**11**), I (**12**); M = Ag, X = NO_3 (**13**)] and $Au_4(\mu\text{-}PP_3)X_4$ [X = Cl (**14**), Br (**15**), I (**16**)] have been prepared by interaction between gold(I) or silver(I) salts and the ligand tris[2-(diphenylphosphino)ethyl]phosphine (PP_3) in the appropriate molar ratio. Microanalysis, mass spectrometry, IR and NMR spectroscopies and conductivity measurements were used for characterization. **1–3** and **4** are ionic dinuclear species containing four-coordinate gold(I) and four/three coordinate silver(I), respectively. Solutions of **10–12** behave as mixtures of complexes in a 2:1 [$Au_2(\mu\text{-}PP_3)X_2$; X = Cl(**6**), Br(**7**), I(**8**)] and 4:1 (**14–16**) metal to ligand ratio. **13** and **15** react with free PP_3 in solution to generate the ionic compounds **4** and **2**, respectively. Complexes **15** and **16**, with four linear PAuX fragments per molecule, were shown by X-ray diffraction to consist of dimeric aggregates *via* close intermolecular gold(I) · · · gold(I) contacts of 3.270 Å (**15**) and 3.184 Å (**16**). The resultant octanuclear systems have an inversion center with two symmetry-related gold(I) atoms being totally out of the aurophilic area and represent a new form of aggregation compared to that found in other halo complexes of gold(I) containing polyphosphines. The luminescence properties of the ligand and complexes, in the solid state, have been studied. Most of the gold systems display intense luminescent emission at room and low temperature. The influence of the halogen on the aurophilic contacts of compounds with a 4:1 metal to ligand ratio results in different photophysical properties, while **15** and **16** are luminescent complex **14** is nonemissive. The luminescence increases with increasing the phosphine/metal ratio affording for complexes **1–3**, without aurophilic contacts, the stronger emissions. Silver complexes **4** and **5** are nonemissive at room temperature and show weaker emissions than gold(I) species at 77 K.

Introduction

The coordination chemistry of the coinage metals has been subjected of investigation for decades due to the wide range of applications of their metal complexes. These metals all display the ability to form attractive nonbonding "metallophilic" interactions that can strongly influence the structure and properties in the resultant materials. Such interactions have been shown to play a significant role in the origin of the luminescent activity, the use of phosphine ligands favoring both the metal centres proximity and the luminescence.[1–6] The interactions are most likely the result of relativistic and correlation effects particularly in the case of gold for which these effects are especially pronounced,[1c,6] leading to compounds with gold–ligand bonds that are shorter than the corresponding silver–ligand bonds.[7] In spite of the preferred linear two-coordinate (by using sterically bulky ligands) and tetrahedral four-coordinate geometries for gold and silver, respectively it is possible to prepare and isolate both silver(I) and gold(I) complexes with varying coordination geometries ranging from linear to tetrahedral.[7a,8–12] The five-coordination[13] has been also reported in a few cases.

The ability of the ligands to act as donors through various coordination modes can give rise to species ranging from simple mononuclear systems to multinuclear clusters and coordination polymers,[8–12] with the tendency of Cu(I), Ag(I) and Au(I) complexes to form clusters and aggregates being a result of metal–metal interactions.[2b–d] Furthermore, subtle modifications to the polymers compositions, as an added methyl group in the 3-position on the pyridyl fragment of an imidazolium N-heterocyclic carbene ligand used in the preparation of Au(I)–Ag(I) coordination polymers, lead to significant variations in structures and luminescence properties.[1e]

An important number of emissive gold(I) systems arise from species containing bridging ligands and aurophilic contacts,[14–16] where the changes in the anionic ligands or neighboring anions can dramatically influence the optical behaviour.[4d,15a,16] Thus, the emission spectra of $[Au_3(\mu\text{-dpmp})_2X](PF_6)_2$

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(dpmp = bis(diphenylphosphinomethyl)phenylphosphine; X = Cl, Br, I), consisting of three Au(I) ions bridged by two dpmp ligands, were entirely different depending on the halide anion with the bromo complex being not luminescent.[16a] The interatomic distance usually observed in compounds with these aurophilic[16b] interactions is on the order of 3.00–3.25 Å[16c] and their strength has been estimated to be in the range of 6 to 8 kcal mol^{-1}.[16d–f] However, using variable temperature ^{31}P-NMR spectroscopy and simulations it was found an aurocarborane 1,1′-$(AuPPh_3)_2$-[2-(1′,2′-$C_2B_{10}H_{10}$)-1,2-$C_2B_{10}H_{10}$] with an unusually strong aurophilic interaction of 11 kcal mol^{-1}. It seems that the electron deficiency of the gold atoms caused by the strong negative inductive effect of the carborane cages is responsible for the stronger interaction in contradiction to other analyses of the nature of gold carboranyl compounds. On the other hand, the complexes prepared by treatment of $[(CH_2)_n(Ph_2PAuO_2CCF_3)_2]$ with 4,4′-bipyridine seem to exist in solution as an equilibrium mixture of linear oligomers and cyclic complexes that when n = 1,3 or 5 consist of luminescent 26-, 30- and 34-membered cationic rings and trifluoroacetate counteranions. The X-ray crystal structure of the weakly emissive solid with $n = 1$ confirms a macrocyclic structure where the geometry about each gold(I) centre is approximately linear and the transannular gold-gold distances are 3.106(1) and 3.084(1) Å.[16g]

Another kind of emissive gold(I) compound containing phosphines was found in three or four coordinate systems without aurophilic contacts. One example consists of Au(I)-based metallocryptates of the type $[Au_2M(\mu\text{-dppn})_3](PF_6)_3$ (M = alkali metal ion, dppn = 2,9-bis(diphenylphosphino)-1,8-naphthyridine), prepared by a template reaction, with structures containing three-coordinate gold(I) that are emissive species when M = Li, Na, K, Cs and that convert into a nonluminescent compound by replacement of gold and M by silver.[17] Other examples correspond to three-coordinate dimeric, $[Au_2(NP_3)_2](BPh_4)_2$ (NP_3 = tris[2-(diphenylphosphino)ethyl]amine) and three-coordinate monomeric, $Au(NP_3)X$, X = PF_6^-,NO_3^-, species with the geometries trigonal planar or distorted tetrahedral and counteranions influencing the optical properties. Thus, the BPh_4^- and PF_6^- salts exhibit yellow luminescence whereas the NO_3^- salt gives a blue luminescence. The luminescence disappears for $Au(NP_3)X$ at room temperature when Au(I) is replaced by Ag(I).[18a] Likewise, the first prepared sigma-bonded gold(I) polymers containing only phosphorus-donor ligands correspond to strongly luminescent three-coordinate gold(I) species with one-dimensional and two-dimensional structures.[18b] However, the compound $[Au(dcpe)_2](PF_6)$ (dcpe = 1,2-Bis(dicylohexylphosphino)ethane) with an approximately tetrahedral AuP_4 structure is nonemissive (solution or solid) while $[Au_2(dcpe)_2](PF_6)_2$ with AuP_3 units shows emission as a solid at 77 K but not at room temperature and $[Au_2(dcpe)_3](PF_6)_2$, luminescent in the solid state, constituted the first example of a gold complex, containing an isolated AuP_3 unit, that emits in solution at room temperature. These data indicate that not only the geometry but also the Au–L bonding and metal to ligand ratios are key factors in Au(I) photophysics.[18c] Finally, Au(I) species of the type $[Au(4\text{-R-dppn})_2]X$ (dppn = 1,8-bis(diphenylphosphino)naphthalene; R = H: X = PF_6, Cl; R = Me: X = PF_6) are examples of tetrahedral four-coordinate compounds with a photoluminescent and electroluminescent behaviour.[18d]

Owing to the scantiness of reports on Au(I) and Ag(I) complexes containing tripodal polyphosphine ligands[19] and with the aim of exploring the role of the halogen (or other anionic ligands or counterions) and the stoichiometry in the structure and photophysical properties of the resultant compounds, here we describe the coordination of the potentially tetradentate tetraphosphine tris[2-(diphenylphosphino)ethyl]phosphine (PP_3) with Ag(I) and Au(I).

Results and discussion

Syntheses

Treatment of a solution of Au(tdg)X (tdg = thiodiglycol = 2,2′-thiodiethanol; X = Cl, Br) and $AgNO_3$ in methanol or AuI and AgCl as solids with dichloromethane solutions of PP_3 in the appropriate stoichiometric ratio gives solutions and/or precipitates of complexes **1–5** and **10–16**. By addition of diethylether and/or water, air-stable solids were afforded in good (85%) or moderate (30–45%) yields. The reaction of **15** and **13** with two equivalents of PP_3 gives **2** and **4**, respectively in solution. Complexes **1**, **4**, **5** and **10** were isolated as dichloromethane solvates. Most of these compounds (**2–5**, **10**,**11**, **14–16**) are white solids. **1** is yellow, **12** grey and **13** beige. Complex **12** was not soluble in DMF and **3** was insoluble in both DMF and DMSO. For each stoichiometry the solubilities in the common organic solvents increase from silver to gold and from chlorides to bromides. With independence of the metal the highest solubilities were found for compounds with a 1:1 stoichiometry.

Characterization

The results of conductivity measurements, mass and far infrared spectra for compounds **1–5** and **10–16** are given in Table 1 and 2 shows the $^{31}P\{^1H\}$NMR data.

Complexes **1**, **4**, **5**, **13** and **14** were previously reported.[19b,c] Solutions of complex **4** consist of $[Ag_2(\mu\text{-}PP_3)_2]^{2+}$ dications, bearing AgP_4 + AgP_3 environments, and NO_3^- counteranions. Complex **5** contains silver(I) bound to three phosphorus atoms and the data for **13** reveal the presence of both AgP_2 + AgP environments with the nitrates acting as ligands.[19–22]

Gold(I) complexes with a 1:1 metal to ligand ratio. Complexes **2** and **3** are isostructural with **1**. These compounds are salts containing a binuclear cation, $[Au_2(\mu\text{-}PP_3)_2]^{2+}$, in which each PP_3 coordinates through three phosphorus atoms to one gold(I) and is acting as a bridging ligand through a terminal phosphorus to the other metal ion. The bridging arms of the PP_3 ligands produce a ten-membered ring that incorporates the two gold ions. Both golds have nearly tetrahedral AuP_4 geometry. The cation retains its binuclear structure in solution. Two halides act as counteranions.[19,20] A comparable behaviour was observed for the tripodal ligand CP_3 (1,1,1-tris(diphenylphosphinomethyl)ethane), by interaction with Au(tdg)Cl, giving not a mononuclear neutral complex but a trinuclear cationic species, $[Au_3(\mu\text{-}CP_3)_2Cl_2]Cl$, with the cation containing both tetrahedral and linear golds.[19a]

Gold(I) complexes with a 3:1 metal to ligand ratio. Complexes **10** and **11** are not conductors in DMF. The solids **10–12** decompose (over 250 °C) without melting. The far infrared spectrum of **10** shows a very strong band in agreement with the presence

Table 1 Conductivities, mass spectra and far infrared data for compounds **1–5** and **10–16**

Compound	Λ(DMF)/Ω^{-1} cm^2 mol^{-1}	MS(L-SIMS)/ESI-MS(+)* m/z (% abundance)	IR (M–X)$^{\#}$ $\nu_{\max}$/cm^{-1}
(**1**)·2CH_2Cl_2	131.8	1522^{a} (8%), 867^{b}(100%)	
2	132.6	1522^{a}(12%), 867^{b}(100%)	
3		1522^{a}(12%), 867^{b}(100%)	
(**4**) CH_2Cl_2	165.7	1344^{a}(31%), 779^{*b}(100%)	1383 vs
(**5**)·0.5CH_2Cl_2	87.0	779 (12%)	185 s
(**10**)·3CH_2Cl_2	4.9	1331^{c}(11.4%), 1134^{d}(7.2%), 1099^{e}(9%)	324 vs
11	9.4	1695^{f}(2%), 1419^{g}(3%), 1143^{h}(4%)	233 s, 217 m, 206 m
12		1839^{f}(10%), 1515^{g}(4%), 1191^{h}(6%)	174 vs, 165 sh
13	101.1	950^{e}(26%), 888^{i}(100%)	1488 m, 1360 s, 1384 vs, 1280 s, 1026 w, 992 w
14	3.3	1563^{c}(8%), 1331^{e}(21.6%), 1134^{j}(5.1%), 1099^{k} (6.8%)	324 vs
15	4.2		232 vs, 219 vs, 207 s
16	3.7		174 vs, 168 sh, 150 w

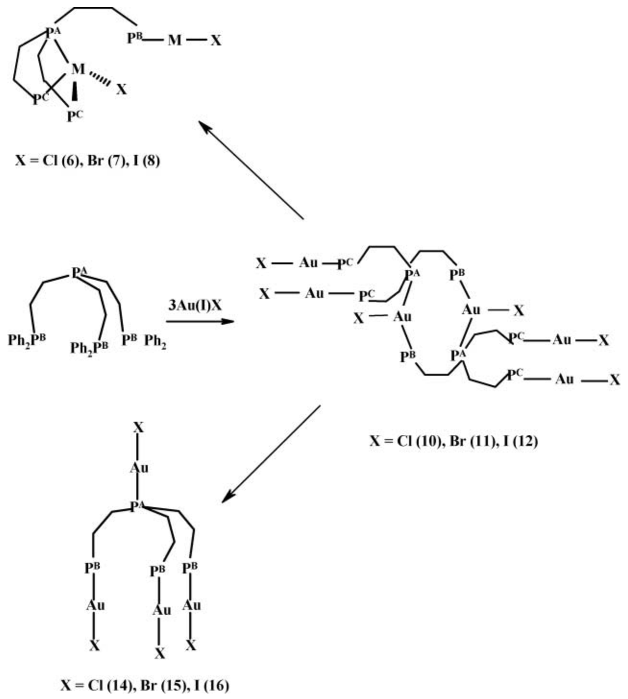
M^+ = Molecular ion, $^{\#}$(M = Au, Ag; X = Cl, NO_3):^{a} ($M^+ - 2X - C_2H_4PPh_2$). ^{b} ($M^+ - 2X - PP_3 - M$). ^{c} ($M^+ - X$). ^{d} ($M^+ - X - M$). ^{e} ($M^+ - 2X - M$). ^{f} ($M^+ - 3X - PP_3 - 2M$). ^{g} ($M^+ - 4X - PP_3 - 3M$). ^{h} ($M^+ - 5X - PP_3 - 4M$). ^{i} ($M^+ - 3X - M$). ^{j} ($M^+ - 2X - 2M$). ^{k} ($M^+ - 3X - 2M$).

Table 2 ^{31}P-{^{1}H}NMR data (r.t.) for complexes **1–5**, **10–16** and for titrations of **13** and **15** with PP_3

Compound	δP^{a}	J(P–P)	Solvent
(**1**)·2CH_2Cl_2	31.9(m)[2P], 24.6(m)[2P], 12.9(m)[4P]	132, 71, 61	$CDCl_3$
2	34.0(m)[2P], 26.6(m)[2P], 15.0(m)[4P]	132, 72, 60	CD_2Cl_2
3	33.9(m)[2P], 25.7(m)[2P], 15.2(m)[4P]	132, 71, 62	CD_2Cl_2
(**4**)·CH_2Cl_2	15.2(br,d)[2P], 8.0(br,d)^{b} [1P],−0.2(dm)[4P], −4.7(br,d)[1P]		CD_2Cl_2
(**4**)·CH_2Cl_2 ^{c}	14.6(dd)[2P], 8.2(br)[1P], −0.3(dm)[4P], −4.8(br)[1P]		CD_2Cl_2
(**4**)·CH_2Cl_2 ^{d}	15.1(dm)[2P], 0.6(dm)[4P]		$CDCl_3$ + CD_3OD
(**5**)·0.5CH_2Cl_2	−3.8(br)[4P]		$CDCl_3$
(**5**)·0.5CH_2Cl_2 ^{c}	15.9(d)[1P], 10.0(d)[1P], −0.5(br)[2P]		CD_2Cl_2
(**10**)·3CH_2Cl_2	**6** + **14**		DMSO-d_6
6	49.7(br)[1P^A], 34.9(d)•[2P^C], 33.0(br,d)[1P^B]	152•	
14	36.9(q)*[1P^A], 34.1(d)*[3P^B]	59*	
11	**7** + **15**		$CDCl_3$
7	50.5(br)[1P^A], 40.0(br,d)•[2P^C], 31.0(br)[1P^B]	158•	
15	38.9(s)[3P^B], 31.0(br,m)[1P^A]		
12	**8** + **16**		$CDCl_3$
8	50.0(br)[1P^A], 43.9(br)[2P^C], 34.1(br)[1P^B]		
16	38.2(d)*[3P^B], 34.1(br)[1P^A]	55*	
13	7.4(br)[4P]		$CDCl_3$ + DMF
13^{c}	10.4(br,d)[2P], 7.6(br,d)[2P]	53	CD_2Cl_2 + DMF
14	31.5(m)[1P^A], 29.3(m)[3P^B]	58	$CDCl_3$ + DMF
15	36.8(q)[1P^A], 35.7(d) [3P^B]	48	DMSO-d_6
16	35.3(d)[3P^B], 33.8(m)[1P^A]	43	CD_2Cl_2
13 + 1 eq. PP_3	**4** + **9**		$CDCl_3$ + DMF
4	12.1(br)[2P], −2.7(br)[4P]		
9	8.1(br)[4P]		
13 + 2 eq. PP_3^{d}	12.5(dm)[2P], −3.0(dm)[4P] (**4**)		$CDCl_3$ + DMF
15 + 1 eq. PP_3	**7** + **2**		$CDCl_3$ + DMSO-d_6
7	47.0(br)[1P^A], 45.1(br,m)[2P^C], 33.5(br)[1P^B]	169	
2	38.0(m)[2P], 28.5(m)[2P], 18.7(m)[4P]	131, 70, 61	
15 + 2 eq. PP_3	37.9(m)[2P], 28.4(m)[2P], 18.6(m)[4P] (**2**)	132, 70, 60	$CDCl_3$ + DMSO-d_6

^{a} [nP] = relative intensities. ^{b} $^1J(^{31}P,^{107/109}Ag)$ = 376/433 Hz. ^{c} $^1J(^{31}P,^{107/109}Ag)$: 343/395 and 194/223 Hz (**4**, 253 K, δ 14.6 dd and −0.3 dm, respectively), 402 (av.) and 395 (av.) Hz. (**5**, 233 K, δ 15.9 d and 10.0 d, resp.), 752 (av.) and 512 (av.) Hz (**13**, 253K, δ 10.4 br and 7.6, resp.). ^{d} 356/410 and 199/229 Hz (**4**, 298 K, δ 15.1 dm and 0.6 dm, resp.), 340/391 and 190/219 Hz (**13** + 2 eq. PP_3, δ 12.5 dm and −3.0 dm, resp.).

of equivalent terminal Au–Cl bonds as expected for a structure containing three linear PAuCl fragments involving terminal phosphorus.[19a] The most abundant peak at highest m/z of **10** can be assigned to a fragmentation of a monomeric species, by loss of one halogen. The three and two bands assigned to the ν(Au–X) vibrations of **11** and **12**, respectively are indicative of non-equivalent terminal Au–X bonds. The peaks at highest m/z for **11** and **12** correspond to tetranuclear fragments, $Au_4(PP_3)X_3$. On this basis, complex **10** is apparently a monomer while **11** and **12** could be dimers. However, the ^{31}P{^{1}H}NMR spectra of the three complexes show a similar dissociative behaviour in solution compatible with a dimeric structure as shown in Scheme 1. Indeed, the high number of resonances found in the spectrum of **10**, recorded in a coordinating solvent as DMSO-d_6, is in agreement with a mixture of species. The quartet at δ 36.9 and the resonance at δ 34.1 (Fig. 1), with approximately relative intensities 1:3 and



Scheme 1 Complexes **10–12** as precursors of compounds **6–8** and **14–16**.

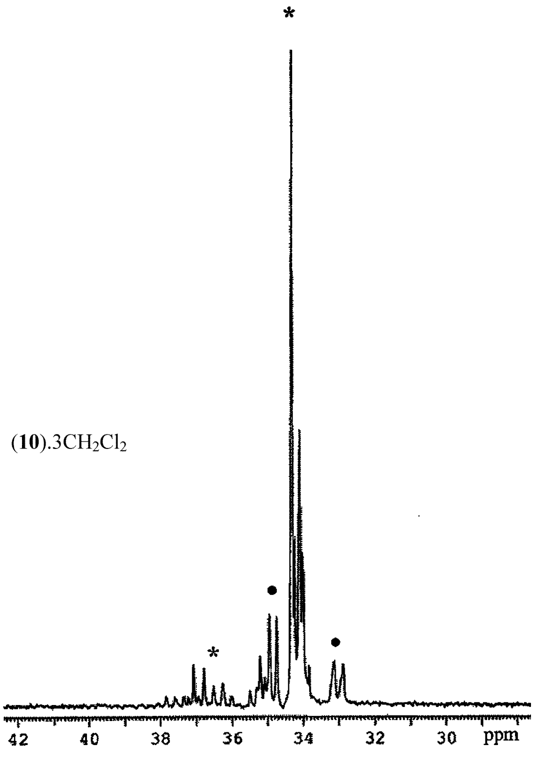


Fig. 1 ^{31}P-{^{1}H} NMR spectrum at room temperature for (**10**)·3CH$_2$Cl$_2$ in DMSO-d$_6$ affording a mixture of **6** (●) and **14** (*).

coupling constants between phosphorus J_{AB} of 59 Hz (*vide infra*), seem to correspond to complex **14** while the signals at δ 34.9 and 33.0 with relative intensities 2:1 and J_{AC} of 152 Hz are assigned to complex **6**. The broad signal of **6** at δ 49.7 (Table 2) is not shown in Fig. 1. Thus, solutions of complex **10** in DMSO appear to give a mixture of compounds **14** and **6**. The signals observed in the ^{31}P{^{1}H}NMR spectra of **11** and **12**, recorded in CDCl$_3$, are also consistent with the presence of mixtures of **7** + **15** and **8** + **16**, respectively. The peaks assigned to the apical phosphorus of **15** and **16** appear now at higher field than those corresponding to the terminal ones [δ 38.9(**11**), 38.2 (**12**)] and are overlapped with the signals at δ 31.0 and 34.1 due to complexes **7** and **8**, respectively. The preparation of crystals of **15** starting from solutions of **11** in DMF/Et$_2$O (eqn (1)) is another evidence of this dissociative process in solution.

$$\underset{\mathbf{11}}{[\mathrm{Au_3(\mu\text{-}PP_3)Br_3}]_2} \xrightarrow{\mathrm{DMF/Et_2O}} \underset{\mathbf{15}}{\mathrm{Au_4(\mu\text{-}PP_3)Br_{4(cryst)}}} + \underset{\mathbf{7}}{\mathrm{Au_2(\mu\text{-}PP_3)Br_{2(sol)}}} \quad (1)$$

According to Scheme 1 the dissolution of **11** would involve a ring-opening process that converts the two vulnerable three coordinate golds into two linear P–Au–Br moieties leading to complex **15** and leaving one (PP$_3$)Au$_2$Br$_2$ fragment that contains two uncoordinated phosphorus and two linear golds. This produces the lone pair cession of the two uncoordinated phosphorus to one linear gold affording complex **7**. It seems that complexes **10–12** do not exist in solution as individual species and the differences observed between **10** and **11–12** could arise from a different form of supramolecular aggregation of the solids. If the solids are formed by aggregates of compounds with 2:1 and 4:1 metal to ligand ratios, we suppose for **10** a form of aggregation that retains the shortest intermolecular contacts of **14**[19c] and joins aurophilic interactions involving the linear fragment of **6**. Likewise, for **11–12** the supramolecular arrangement would include aurophilic contacts due to **15** and **16** (*vide infra*) and those involving linear PAuX fragments of complexes **7** and **8**, respectively.

Gold(I) complexes with a 4:1 metal to ligand ratio. Complexes **14–16** are neutral species in DMF. The peak at highest *m*/*z* value in the LSI mass spectrum of **14** corresponds to the loss of one halogen from the molecular ion. The bands observed in the far infrared spectrum of **14–16** are consistent with the presence of terminal M–X bonds.[23] The ^{31}P{^{1}H}NMR spectrum consisting of two signals with relative intensities 1:3 (A:B) (*vide infra*) and the phosphorus coupling constants J_{AB} ranging from 58 to 43 Hz support the structures shown in Scheme 1. It should be noted that solutions in CD$_2$Cl$_2$ of the iodo derivative **16** exhibit an inversion of the resonances due to the apical (δ 33.8) and terminal phosphorus (δ 35.3) compared to complexes **14** (CDCl$_3$ + DMF) and **15** (DMSO-d$_6$) with the different coordination ability of the solvents being probably the reason of this fact. This inversion (just found for solutions of **11** and **12** in CDCl$_3$) was also previously observed for **14** in CDCl$_3$.[19c]

Crystallography of 14–16. The structure proposed in solution for complex **14** coincides with that one found in the solid state by X-ray diffraction.[19c]

In this work we afforded crystals of (**15**)·2H$_2$O and (**16**)·2DMSO that were studied by X-ray crystallography.† Single crystals of (**15**)·2H$_2$O were obtained by slow evaporation of a DMF/Et$_2$O solution of **11** (*vide supra*) while crystals of (**16**)·2DMSO appeared by recrystallization from solutions of **16** in DMSO. Perspective views of the molecular structures and numbering schemes are shown in Fig. 2 and 3. Crystallographic data are given in Table 3 and selected bond lengths and angles are listed in Table 4.

In both cases the asymmetric units are made up of neutral tetranuclear complexes where four Au–X moieties are bridged by

Table 3 Summary of crystal parameters, data collection and refinement for (**15**)·2H_2O and (**16**)·2DMSO

Complex	(**15**)·2H_2O	(**16**)·2DMSO
Empirical formula	$C_{42}H_{46}P_4Br_4O_2Au_4$	$C_{92}H_{108}P_8I_8O_4S_4Au_8$
Formula weight	1810.14	4244.72
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal size/mm	0.28 × 0.09 × 0.08	0.24 × 0.07 × 0.06
Color/habit	Colorless/prisms	Yellow/needles
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a/Å	25.795(9)	25.449(5)
b/Å	24.108(9)	23.715(5)
c/Å	20.483(7)	20.506(5)
α/°	90	90
β/°	113.905(6)	112.735(5)
γ/°	90	90
Volume/Å^3	11645(7)	11414(4)
Z	8	4
Calculated density/Mg m^{-3}	2.065	2.470
Absorption coefficient/mm^{-1}	12.930	12.633
F(000)	6608	7728
θ range for data collection/°	1.21 to 22.32	1.22 to 24.72
Index ranges	$-27 \le h \le 25$	$-29 \le h \le 27$
	$0 \le k \le 25$	$0 \le k \le 27$
	$0 \le l \le 21$	$0 \le l \le 24$
Reflections collected	29264	30837
Independent reflections	7282 [$R_{int} = 0.0738$]	9967 [$R_{int} = 0.0715$]
Max. and min. transmission	0.4244 and 0.1225	0.5178 and 0.1515
Data/restraints/parameters	7282/42/439	9711/0/520
Goodness of fit on F^2	0.966	1.018
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0572$	$R_1 = 0.0812$
	$wR_2 = 0.1940$	$wR_2 = 0.2345$
Largest diff. peak and hole/e Å^{-3}	1.903 and −2.623	4.268 and −4.104

Table 4 Selected distances (Å), aurophilic contacts (Å)[a] and angles (°) for complexes (**15**)·2H_2O and (**16**)·2DMSO

Complex	(**15**)·2H_2O	(**16**)·2DMSO
Au(1)–P(1)	2.242(6)	2.236(7)
Au(2)–P(2)	2.152(2)	2.242(8)
Au(22)–P(2)	2.409(2)	
Au(3)–P(3)	2.223(8)	2.236(7)
Au(4)–P(4)	2.240(7)	2.255(7)
Au(1)–X(1)	2.418(3)	2.427(3)
Au(2)–X(2)	2.391(2)	2.400(6)
Au(22)–Br(22)[b]	2.378(9)	
Au(3)–X(3)	2.399(4)	2.294(3)
Au(4)–X(4)	2.412(3)	2.410(3)
Au(1)–Au(4_7)[a]	3.270(2)	3.184(2)
P(1)–Au(1)–X(1)	172.4(2)	172.2(2)
P(2)–Au(2)–X(2)	172.5(8)	171.4(4)
P(2)–Au(22)–Br(22)	177.1(5)	
P(3)–Au(3)–X(3)	179.4(2)	179.2(2)
P(4)–Au(4)–X(4)	175.4(2)	174.7(2)

[a] Aurophilic contacts (P^A = apical phosphorus, P^B = terminal phosphorus) for: (**14**)·2.8CH_2Cl_2·Et_2O [Au(P^A)–Au(P^B) = 3.061 Å (intermolecular interaction involving one asymmetric unit), Au(P^B)–Au(P^B) = 3.140 Å (intermolecular interaction involving two different asymmetric units)]; (**15**)·3H_2O and (**16**)·2DMSO involving Au(P^A)–Au(P^B) between two symmetry-related molecules. [b] Au(22) and Br(22) are disordered atoms.

the tetraphosphine generating nearly linear P–Au–X arrangements in agreement with the structures proposed in solution.

The averages of the Au–P [2.253(9) Å (**15**); 2.242(7) Å (**16**)] bond lenghts are in the expected range for compounds containing nearly linear P–Au–fragments,[10b,19a,24,25e] very close to those found for **14**[19c] and shorter upon reduction of the coordination number than the average Au–P distances found for **1**.[19] These Au–P bond lenghts are also shorter, as expected,[7] than the average of the Ag–P distances observed for the infinite chain structures of $Ag_2(CP_3)X_2$ (CP_3 = 1,1,1-tris(diohenylphosphinomethyl)ethane; X = Cl: 2.443(3) Å, X = Br: 2.458(11) Å, X = I: 2.503(7) Å)[19b] The shortest Au–P distance for **15** (2.152(2) Å) corresponds to Au(2)–P(2) while for **16** the Au(1)–P(1) and Au(3)–P(3) distances are slightly shorter (2.236(7) Å) than Au(2)–P(2) (2.242(8) Å) and Au(4)–P(4) (2.255(7) Å).

The average for Au–Br distances in **15** (2.400(5) Å) is within the expected values for this type of bonds in linear P–Au–Br moieties with the shortest bond lengths (2.391 Å) corresponding to Au(2)–Br(2). However, the average for Au–I (2.408(4) Å, **16**) bonds is smaller than in other trigold complexes containing triphosphines[19a,24,25a] with the shortest distance (2.294(3) Å) involving Au(3) and I(3). The close to linear X–Au–P arrangements [av. 175.4(3)° (**15**), 174.4(2)° (**16**)] are in accordance with those observed in Au_3(μ-CP_3)Br_3 (173.1(1)°),[19a] Au_3(μ-tppm)I_3 [tppm = tris(diphenylphosphino)methane, 168.3(1)°][24] or Au_3(μ-CP_3)I_3 (174.5(3)°).

An interesting feature of these structures is the presence of pairs of symmetry-related molecules with each one belonging to a different asymmetric unit. This contrast to the structure of **14** previously reported[19c] that showed an asymmetric unit containing two molecules. The AuX moieties bridged by the apical and one dangling phosphorus of each component [Au(1)–Au(4_7)

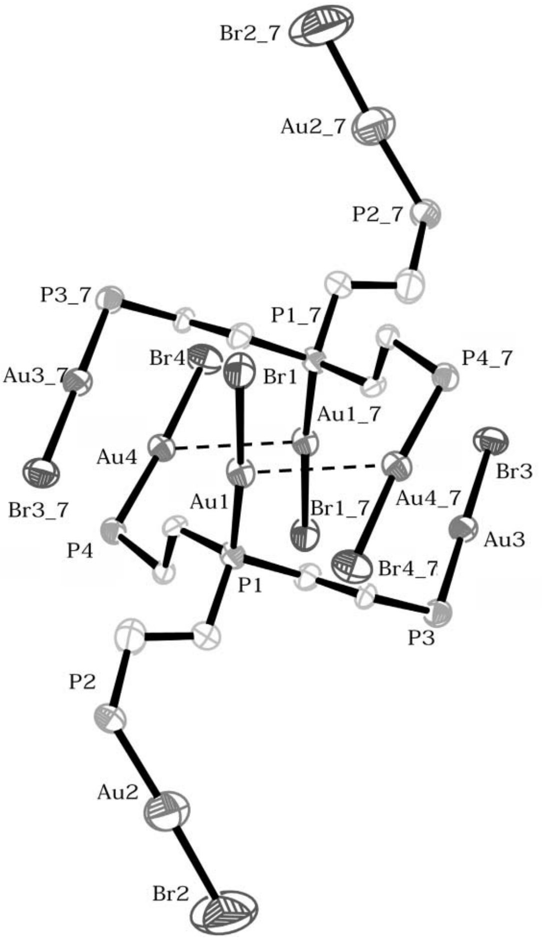


Fig. 2 Perspective view of two symmetry-related molecules for complex **15** showing short Au(1)–Au(4_7) and Au(4)–Au(1_7) contacts. The symmetry generations of atoms are labelled with _7s. Phenyl rings were omitted for clarity.

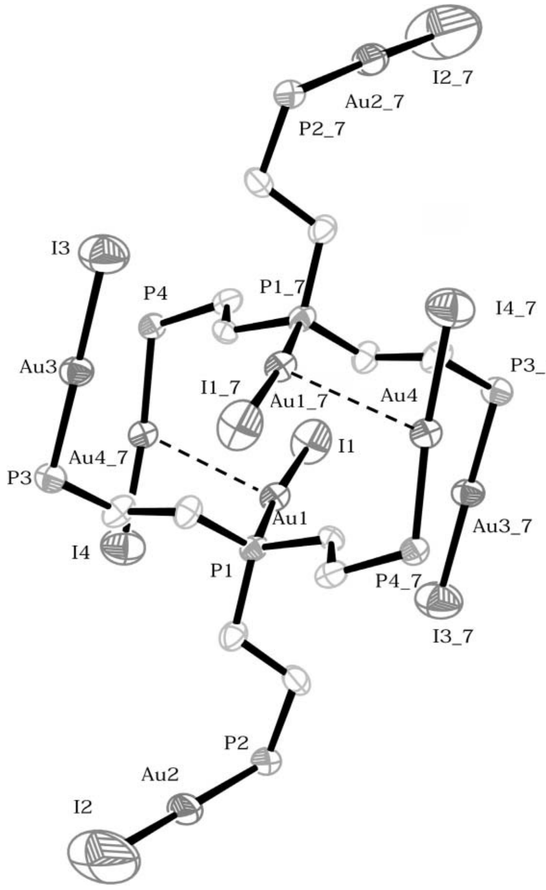


Fig. 3 Perspective view of two symmetry-related molecules for complex **16** showing short Au(1)–Au(4_7) and Au(4)–Au(1_7) contacts. The symmetry generations of atoms are labelled with _7s. Phenyl rings were omitted for clarity.

and Au(1_7)–Au(4)] of these dimeric aggregates are crossed giving close intermolecular Au···Au contacts of 3.270(2) Å for **15** and 3.184(2) Å for **16**. A third PAuX fragment of each molecule is relatively close to the aurophilic region without affording short contacts (3.914 Å for **16**). The fourth arm of each phosphine attached to the Au(2)–X(2) or Au(2_7)–X(2_7) fragment is totally out of the clustering pattern excluding any participation in aurophilic interactions. The gold-gold contacts[26] are slightly longer than those found between molecules for **14**[19c] involving gold atoms bound to one apical and one terminal phosphorus in the same dimeric asymmetric unit [3.061(5) Å] and to terminal phosphorus of molecules belonging to different asymmetric units [3.140(5) Å] (Table 4). The interactions are also longer than the intermolecular attractions of 3.048 Å and 3.107(7) Å found for complexes Au_3(μ-tripod)Br_3[19a] and Au_3(μ-CP_3)Br_3,[25a] respectively although shorter than the intramolecular distances observed in the trinuclear derivative [Au_3(μ-dpmp)Cl_3] (dpmp = bis(diphenylphosphinomethyl)phenylphosphine) (3.3709(4) Å)[10b] or in [Au_2(μ-dppm)Cl_2] [dppm = bis(diphenylphosphino)methane, 3.351(2) Å].[25b] All intramolecular gold-gold separations for **14–16** (5–12 Å) correspond to non-bonded Au···Au distances in contrast with the short intramolecular aurophilic contacts observed for Au_3(μ-CP_3)Cl_3 (3.091 Å)[25c] and [Au_4(μ-dpmp)$_2Cl_2$](CF_3SO_3)$_2$ (3.103(2), 3.106(2) Å).[22b]

Thus, the crystal structures of **15** and **16** constitute a new example of supramolecular aggregation compared with **14** and other gold(I) compounds containing tripodal ligands of the type Au_4(μ-PP_3)$(SR)_4$ (RS = quinoline-2-thiolate) or Au_3LX_3 (L = NP_3, CP_3; X = Cl, Br, I) reflecting the influence of the halogen. Crystals of Au_3(μ-NP_3)X_3 (X = Cl, Br)[25a] are aggregated into layers with the shortest intermolecular distances corresponding to Au···X instead of Au···Au contacts while the molecules of Au_3(μ-NP_3)I_3 are linked up through close Au···Au interactions involving two of the three P–Au–I linear fragments. However, complexes Au_4(μ-PP_3)$(SR)_4$ and Au_3(μ-CP_3)X_3 (X = Cl, I) do not show aggregation, exibiting only intramolecular gold-gold bonds, and the crystals of Au_3(μ-CP_3)Br_3 are made up of dimeric aggregates with all phosphorus atoms involved in aurophilic (one inter- and two intramolecular) contacts.[19a,25c,d]

Transition from high to low metal to ligand ratios

It is known that the binuclear cation of complex **1** is resistant to reaction with the nucleofile azide and thiocyanate but reacts readily with Me_2SAuCl to form the neutral compound **14** *via* a ring-opening process.[19c]

In this work we report the reactivity *versus* PP_3 of the complexes **15** and **13**, followed by $^{31}P\{^1H\}NMR$, to give the ionic species **2** and **4**, respectively (Table 2).

When complex **15** reacts in $CDCl_3/DMSO-d_6$ with one equivalent of PP_3 there appear six resonances assigned to a mixture of compounds **2** and **7**. The signal at δ 45.1 that allows a coupling constant between phosphorus J_{AC} of 169 Hz is attributable, together with the resonances at δ 47.0 and 33.5, to complex **7** while the remaining multiplets correspond to complex **2** (eqn (2)).

$$\underset{\mathbf{15}}{2\ Au_4(\mu\text{-}PP_3)Br_4} + 2\ PP_3 \xrightarrow[\text{-2Au(I)Br}]{CDCl_3/DMSO\text{-}d_6} \underset{\mathbf{2}}{[Au_2(\mu\text{-}PP_3)_2]Br_2} + \underset{\mathbf{7}}{2\ Au_2(\mu\text{-}PP_3)Br_2} \quad (2)$$

It should be noted that the reaction occurs in a 2:2 stoichiometric ratio instead of the expected 1:1 ratio to give complex **7** ($Au_4(\mu\text{-}PP_3)Br_4 + PP_3 \rightarrow 2\ Au_2(\mu\text{-}PP_3)Br_2$). With the second addition of ligand the signals due to **7** disappear (eqn (3)).

$$\underset{\mathbf{15}}{2\ Au_4(\mu\text{-}PP_3)Br_4} + 4\ PP_3 \xrightarrow[\text{-2Au(I)Br}]{CDCl_3/DMSO\text{-}d_6} \underset{\mathbf{2}}{3\ [Au_2(\mu\text{-}PP_3)_2]Br_2} \quad (3)$$

Therefore, the conversion of the stoichiometry 4:1 into 1:1 by interaction of **15** with PP_3 takes place previous formation of **7** (2:1) seeming to confirm the non-existence of complex **11** (3:1 stoichiometry) in solution (*vide supra*). Subsequent additions of phosphine lead to the presence of **2**, as predominant species, in coexistence with free and oxidized PP_3 and a new complex (detected by ESI-MS) corresponding to a 1:2 gold to phosphine ratio.

A similar behaviour was observed for **13** in $CDCl_3/DMF$. The first equivalent of ligand seems to give a mixture of **4** and **9** ($Ag_2(\mu\text{-}PP_3)(NO_3)_2$) and with the second addition of PP_3 complex **4** is the only species formed. Subsequent additions of PP_3 give complex **4** in coexistence with free and oxidized phosphine.

Photoluminescence studies

In order to investigate the correlation between structures and visible light emission upon UV excitation the solid-state, emission and excitation spectra at 298 and 77 K for the isolated complexes and the tetraphosphine have been determined, and the results are summarized in Table 5 and Figs. 4 and 5. The emission of PP_3 at room and low temperatures in the visible range, that occurs at higher energies than in complexes, can be related to π–π* phenyl ring transitions as observed for the linear triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine (P_3).[22a] For complexes the luminescence arises from the ligands, the geometry to the metal centre or the presence of intermetallic interactions.

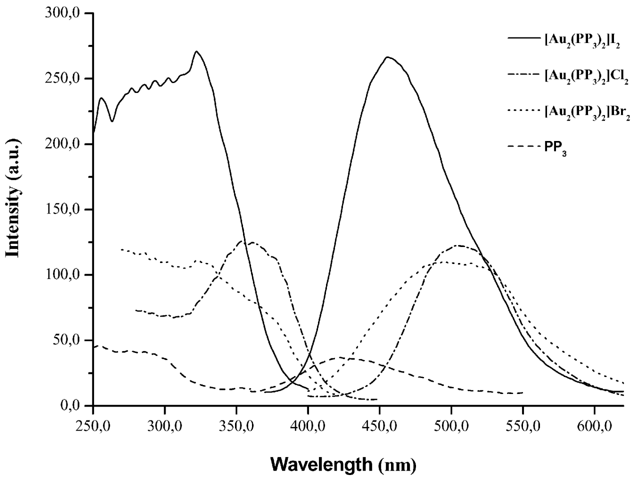


Fig. 4 77 K solid-state excitation and emission spectra of the tetraphosphine (-·-·-·) and complexes **1** (---) and **2** (· · ·) and **3** (—), using a 1% intensity atenuator.

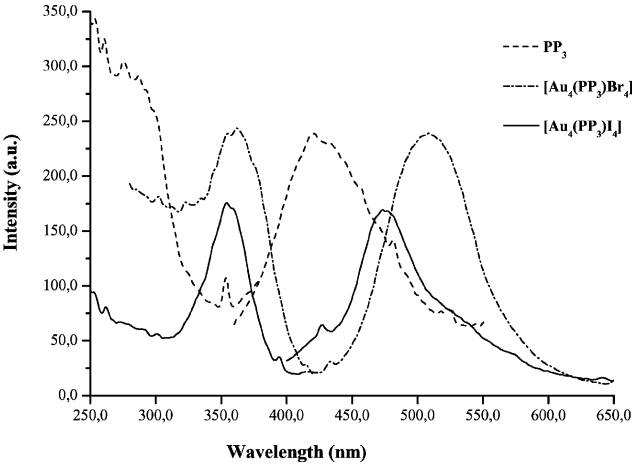


Fig. 5 Solid-state excitation and emission spectra of the tetraphosphine (-·-·-·) and complexes **15** (---) and **16** (—) at 77 K.

Table 5 Emission and excitation maxima (in nm) measured for the tetraphosphine and complexes **1–5**, **10–12** and **15–16** in the solid state at 298 and 77 K

Complex	Excitation 298 K	Emission 298 K	Excitation 77 K	Emission 77 K
PP_3	275–300	423	250–300	423
(**1**)·$2CH_2Cl_2$	385	518	354	504
2	280–340	527	280–325	495
3	342	475 (sh); 513	280–325	455
(**4**)·CH_2Cl_2	—	—	310	482
(**5**)·$0.5CH_2Cl_2$	—	—	280–322	444
(**10**)·$3CH_2Cl_2$	352	482; ~530 (sh)	333	469
11	379	506	354	495
12	324; 368	537	330; 375	563
			341	460 (sh); 562
15	310–360; 380	521; ~580 (sh)	362	509
16	—	—	354	473

While Au(I) complexes (excluding **16** that emits only at room temperature) are luminescent both at room and low temperatures, compounds containing Ag(I), harder than Au(I), only luminesce at 77 K. The Au(I) compounds here reported are luminescent in all stoichiometries studied, however the only Ag(I) luminescent complexes were those corresponding to a 1:1 metal to ligand ratio at 77 K. For gold(I) luminescence increases with increasing the phosphine/metal ratio. On the contrary, the gold(I) complexes containing isolated AuP_3 units and the ligand dcpe = 1,2-Bis(dicyclohexylphosphino)ethane are emissive, in the solid state, for a 1:1 ($[Au_2(dcpe)_2](PF_6)_2$) and 3:2 ($[Au_2(dcpe)_3](PF_6)_2$ phosphine/metal ratio and nonemissive in case of a 2:1 ratio ($[Au(dcpe)_2](PF_6)$).[18c] According to the structures shown in Scheme 1 the only difference between complexes **1–3** seem to come from the counteranions with the emission energy at 77 K increasing from Cl to Br to I (Fig. 4). At room temperature the emission energy decreases from Cl to Br, increases from Br to I and is accompanied with a shoulder at 475 nm for **3**. This significant effect of the counterion on the solid state emission of binuclear gold(I) phosphine complexes was previously reported.[15a] It was found a correlation between emission and the distance of the negative charge from the Au atoms, resulting that the emission band red-shifts as the distance decreases. For **1–3** at 77 K it seems that the distance increases going down on the halogens group. On the other hand, taking into account the large Au $\cdots$ Au intermolecular distance found by X-ray diffraction for complex **1** (6.175 Å) the emission maxima of complexes **1–3** (with AuP_4 arrangements) could be attributed to a phosphine transition modified by the gold(I) centre, as described for other tetrahedral four-coordinate gold(I) complexes.[3b] Complex **4**, containing three and four-coordinate Ag(I) and nitrate as counterion, gives a weaker emission compared to **1–3** and at higher energy than complexes **1** and **2** with chloro and bromo counterions, respectively. The silver chloro complex **5** emits at higher energy than the nitrate, **4**.

Likewise, systematic changes occur with variation of the halide ligand X in gold(I) compounds showing metal/ligand ratios from 3 to 4. The emission energies decrease from Cl to Br to I in complexes with 3:1 gold to phosphine ratios and increase in those with a 4:1 ratio (Fig. 5). The only nonemissive gold(I) system was the chloro complex $Au_4(\mu\text{-}PP_3)Cl_4$ (**14**). Thus the supramolecular arrangement of the solids (**14–16**), with important contribution of the halides and giving different types of aurophilic interactions (*vide supra*), seems to influence their properties.

In complexes with a 4:1 metal to ligand ratio the type of aurophilic Au $\cdots$ Au interactions is suggested as the source for their visible emission that blue-shifts as the halide X is changed from Br to I, in good agreement with other emitting mononuclear gold(I) compounds.[4d] The luminescence disappears if gold(I) is replaced by other metals as Pd(II) or Pt(II) affording heteronuclear systems $[MAu(PP_3)X_2]X$ and $MAu_2(PP_3)X_4$ (M = Pd, Pt; X = Cl, Br, I) with linear PAuX arrangements and distorted square-planar M(II) centres.[19d] The opposite red-shifts observed for emissions of complexes with a 3:1 gold to phosphine ratio (**10–12**) could be attributed to the presence of not only linear geometries for gold(I) according to the structures proposed. The wavelength-dependent emission spectra observed for **10–12** at low temperature are in agreement with those previously found for $[Au_3(\mu\text{-dpmp})(\mu\text{-}S_2CN(CH_2Ph)_2)Cl]CF_3SO_3$[10b] and for aggregates containing gold(I) chains in $[Au(S_2CN(C_5H_{11})_2)]_2$[25f] with complex **12** exhibiting two emission and excitation spectra at 77 K.

Conclusions

By synthetic control of the stoichiometry it was possible to prepare the series of gold(I) complexes $[Au_2(\mu\text{-}PP_3)_2]X_2$, $Au_n(\mu\text{-}PP_3)X_n$ (n = 3, 4) X = Cl, Br, I and silver(I) $[Ag_2(\mu\text{-}PP_3)_2](NO_3)_2$, $Ag(PP_3)Cl$, $Ag_3(\mu\text{-}PP_3)(NO_3)_3$. The gold(I) complexes in a 1:1 stoichiometric ratio are binuclear ionic systems with AuP_4 tetrahedral arrangements to the metal. The structural data for the silver(I) compound in a 1:1 ratio indicate the existence as a ionic system that consists of dications $[Ag_2(\mu\text{-}PP_3)_2]^{2+}$ with three- and four-coordination to the metal and NO_3^- counterions. Complexes prepared in 3:1 and 4:1 metal to ligand ratios are neutral species. The solutions of gold(I) complexes with a 3:1 stoichiometry behave as mixtures of compounds with a 2:1 and 4:1 gold to phosphine ratio. The complexes $Au_4(\mu\text{-}PP_3)Br_4$ and $Ag_3(\mu\text{-}PP_3)(NO_3)_3$ react in solution with two equivalents of PP_3 to form the salts $[Au_2(\mu\text{-}PP_3)_2]Br_2$ and $[Ag_2(\mu\text{-}PP_3)_2](NO_3)_2$, respectively. Gold(I) adopts a nearly linear geometry in all complexes prepared with a 4:1 metal to ligand ratio. The phosphine, the silver(I) complexes with 1:1 stoichiometry and most of the gold systems are luminescent in the solid state. The luminescence found in $Au_4(\mu\text{-}PP_3)X_4$ (X = Br, I) whose X-ray crystal structure confirm the presence of linear PAuX fragments is attributable to the type of metallophilic interactions. The structures consists of an unusual type of dimeric aggregates, *via* close aurophilic contacts, that differs from the supramolecular architecture found for $Au_4(\mu\text{-}PP_3)Cl_4$, a nonemissive complex. However, the stronger emission observed for complexes $[Au_2(\mu\text{-}PP_3)_2]X_2$ (X = Cl, Br, I) with tetrahedral gold(I) and without aurophilic contacts seem to arise from the phosphine ligand modified by the metal centre.

Experimental

General procedures

Dichloromethane was redistilled under nitrogen over $CaCl_2$. Gold iodide was purchased from Strem Chemicals, tris[2-(diphenylphosphino)ethyl]phosphine, silver chloride and 2,2′-thiodiethanol from Aldrich, potassium bromide from Panreac, silver nitrate from Analema and gold metal from S.E.M.P.S.A. Microanalyses were performed on a Fisons Instrument EA 1108 CHNS-O. Liquid Secondary-Ion Mass Spectra (LSI MS) were obtained in a Micromass Autospec spectrometer using 3-nitrobenzyl alcohol as the matrix. Infrared spectra were recorded at ambient temperature as KBr pellets (4000–400 cm^{-1}) and Nujol mulls (500–100 cm^{-1}) on a Nicolet IMPACT 400 with a DTGS detector and a Mattson Cygnus 100 spectrophotometer. The bands are reported as vs = very strong, s = strong, m = medium, sh = shoulder, a = asymmetric vibration, s = symmetric vibration. ^{31}P {^1H} NMR spectra and the ^{109}Ag NMR spectrum were recorded on a Bruker AMX500 spectrometer at 202.46 MHz and 23.31 MHz, respectively. Chemical shifts are reported relative to external standard 85% H_3PO_4 (^{31}P) and a saturated solution of $AgNO_3$ in D_2O (^{109}Ag); δ = chemical shift in ppm; s = singlet, d = doublet, dd = doublet of doublets, dm = doublet of multiplets, m = multiplet, br = broad signal; J = coupling constant in hertzs.

Conductivities were measured at 25 °C using 10^{-3} M solutions in DMF on a WTW model LF-3 instrument. Emission and excitation spectra were measured in the solid state as finely pulverized KBr mixtures at room temperature and 77 K with a Perkin-Elmer LS-50B spectrofluorometer and using a 1% intensity atenuator when required.

Preparations and titrations. Preparation of Au(tdg)Cl

Solutions of Au(tdg)X were prepared *in situ* following the procedures previously described.[26]

Preparation of $[Au_2(\mu\text{-}PP_3)_2]X_2$ [X = Br (2), I (3)]. Solutions of Au(tdg)X (0.087 g, 0.443 mmol in Et_2O, X = Br) or AuI as solid (0.111 g, 0.347 mmol) were added to a solution of PP_3 (0.297 g, 0.443 mmol for X = Br; 0.233 g, 0.347 mmol for X = I) in dry CH_2Cl_2 (10–20 mL). The resultant mixtures were stirred for ~24 h at room temperature (when X = I in an ice bath). After that solvents were partially removed *in vacuo* to leave precipitates that were treated with H_2O (X = Br) or Et_2O (X = I). The final solids were filtered off and dried in vacuo. Λ(DMF), MS and IR data are shown in Table 1 and the $^{31}P\{^1H\}$ NMR resonances are given in Table 2. **2**: Yield: 60%. Color: white, mp 160 °C. Found: C, 52.8; H, 4.5. $C_{84}H_{84}P_8Au_2Br_2$ requires: C, 53.2; H, 4.5. **3**: Yield: 45%. Color: white, mp 271 °C. Found: C, 50.3; H, 4.3. $C_{84}H_{84}P_8Au_2I_2$ requires: C, 50.7; H, 4.2.

Preparation of $Au_3(\mu\text{-}PP_3)X_3$ [X = Cl (10), Br(11), I(12)]. Solutions of Au(tdg)X (0.203 g, 1.029 mmol in MeOH, X = Cl; 0.149 g, 0.756 mmol in Et_2O, X = Br) or AuI as solid (0.228 g, 0.703 mmol) were added to a solution of PP_3 (0.230 g, 0.343 mmol for X = Cl; 0.169 g, 0.252 mmol for X = Br; 0.157 g and 0.235 mmol for X = I) in dry CH_2Cl_2 (12–15 mL). Precipitates were obtained after stirring the reaction mixtures for 24 h at room temperature (when X = I in an ice bath). Unreacted AuI was removed by decantation and in this case Et_2O was added for precipitation. The solids were filtered off and **10** and **11** were stirred with H_2O. Final products were filtered off and dried in vacuo. Λ(DMF), MS and IR data are shown in Table 1 and the $^{31}P\{^1H\}$ NMR resonances are given in Table 2. (**10**)·$3CH_2Cl_2$: Yield: 60%. Color: white, mp 265 °C (dec). Found: C, 33.6; H, 3.1. $C_{45}H_{48}P_4Au_3Cl_9$ requires: C, 33.3; H, 3.0. **11**: Yield: 85%. Color: white, mp 253 °C (dec). Found: C, 33.1; H, 2.9. $C_{84}H_{84}P_8Au_6Br_6$ requires: C, 33.6; H, 2.8. **12**: Yield: 77%. Color: grey, mp 285 °C (dec). Found: C, 30.6; H, 2.8. $C_{84}H_{84}P_8Au_6I_6$ requires: C, 30.7; H, 2.6.

Preparation of $Au_4(\mu\text{-}PP_3)X_4$ [Br (15), I(16)]. Solutions of Au(tdg)X (0.314 g, 1.596 mmol in Et_2O, X = Br) or AuI as solid (0.198 g, 0.612 mmol) were added to a solution of PP_3 (0.268 g, 0.399 mmol, X = Br; 0.103 g, 0.153 mmol, X = I) in dry CH_2Cl_2 (10–15 mL). The reaction mixtures were stirred (for 24 h, X = Br; 30 min, X = I) at room temperature (when X = I in an ice bath). The solvents were removed *in vacuo* for X = Br and Et_2O was added for precipitation when X = I. Solids were treated with H_2O, filtered off and dried in vacuo. Λ(DMF), MS and IR data are shown in Table 1 and the $^{31}P\{^1H\}$ NMR resonances are given in Table 2. **15**: Yield: 30%. Color: white, mp 257 °C (dec). Found: C, 28.8; H, 2.7. $C_{42}H_{42}P_4Au_4Br_4$ requires: C, 28.3; H, 2.4. **16**: Yield: 60%. Color: white, mp 280 °C (dec). Found: C, 26.0; H, 2.2. $C_{42}H_{42}P_4Au_4I_4$ requires: C, 25.6; H, 2.1.

Titrations of complexes 13 and 15 with PP_3. To a solution of **13** and **15** in DMF and DMSO-d_6, respectively, solutions of PP_3 in $CDCl_3$ were added in different stoichiometric ratios. The ^{31}P-$\{^1H\}$ NMR spectra were recorded after each addition. The results are given in Table 2.

Crystal structure determination of 15 and 16. Colorless prisms of (**15**)·$2H_2O$ and yellow needles of (**16**)·2DMSO were mounted on glass fibers and used for data collection. Crystals data were collected at 293(2) K, using a BRUKER SMART CCD 1000 diffractometer. Graphite monochromated MoKα radiation was used throughout. The data were processed with SAINT[27] and empirical absorption correction was made using SADABS.[28] The structures were solved by direct methods using the program SIR-92[29] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[30] Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model. Hydrogen atoms of water molecules were not placed for (**15**)·$2H_2O$ and the oxygens were refined at partial occupancy of 60/40% for O(1 W)/O(3 W) and 70/30% for O(2 W)/O(4 W), respectively. One of the gold and one of the bromine atoms of complex (**15**)·$2H_2O$ are subjected to a two-fold disorder, the atoms Au(2), Au(22), Br(2) and Br(22) were refined with a half occupancy factor. Moreover, in both structures some of the phenyl rings were fitted as regular hexagons. Atomic scattering factors were obtained with the use of International Tables for X-ray Crystallography.[31] Molecular graphics were obtained from ORTEP-3 for Windows.[32]

Acknowledgements

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