Synthesis of homo- and hetero-polynuclear coinage metal complexes of 2-(diphenylphosphino)aniline

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The reaction of the asymmetric ligand 2-(diphenylphosphino)aniline (PNH_2) with gold(I), silver(I) or copper(I) substrates in various molar ratios leads to the complexes $[M(PNH_2)_2]A$ (M = Au, A = TfO (**1**); M = Ag, A = TfO (**2**), ClO_4 (**3**); M = Cu, A = TfO (**4**)), the homodinuclear derivatives $[M(PNH_2)]_2A_2$ (M = Ag, A = TfO (**7**), ClO_4 (**8**); M = Cu, A = TfO (**9**)) or $[M(PNH_2)_3]A$ (M = Au, A = TfO (**12**); M = Ag, A = ClO_4 (**13**); M = Cu; A = TfO (**14**)). Reaction of $[AuCl(PNH_2)]$ with $AgClO_4$ (1:1) in acetone causes the ligand to condense with the solvent, resulting in the synthesis of $[Au(PN=CMe_2)]_2(ClO_4)_2$ (**5**). Treatment of the gold(I) compound **1** with the same silver(I) or copper(I) starting materials as before gives the heteronuclear species $[AuM(PNH_2)_2](TfO)_2$ (M = Ag (**10**); M = Cu (**11**)). The optical properties of some of these complexes have been studied and the crystal structures of compounds **5**, **10** and **12** have been determined by X-ray diffraction.

Introduction

Polynuclear P-, N- or S-donor ligands have been usually employed in the synthesis of a broad diversity of polynuclear species that, in the case of gold, may present interesting applications, such as chemotherapy, diagnostics, catalysis, electron microscopy or surface technology.[1–5] A number of complexes of W, Ni, Pd, Pt, Rh, Os and Re containing the bidentate P,N-donor ligand 2-(diphenylphosphino)aniline (PNH_2) have been described;[6–11] in most of them PNH_2 acts as a bidentate chelating ligand, and the nitrogen atom is sometimes deprotonated. In contrast, only a few derivatives of PNH_2 with group 11 metals have been reported to date,[12] all of them being mono- or homopolynuclear species in which the proposed geometry at the metal ion is invariably linear for gold(I) or tetrahedral for copper(I) or silver(I).

In this paper we describe the synthesis of some mononuclear and homo- or hetero-polynuclear complexes of PNH_2 with group 11 metal centres that could display M–M or M–M′ interactions or a trigonal-planar geometry around the metal ion. It should be borne in mind that metal–metal interactions or tricoordination have been shown to be responsible for interesting optical properties, such as luminescence, in a large number of gold(I) compounds[13] and thus some of the complexes we have synthesized might also be expected to be luminescent materials.

Results and discussion

The reaction of the free ligand PNH_2 with the appropriate M(I) precursor (2 : 1 molar ratio) $[Au(tht)_2]TfO$ (tht = tetrahydrothiophene; TfO = trifluoromethylsulfonate), AgTfO, $AgClO_4$ or $[Cu(NCMe)_4]BF_4$ leads to the synthesis of the mononuclear complexes $[M(PNH_2)_2]A$ (M = Au, A = TfO (**1**); M = Ag, A = TfO (**2**), ClO_4 (**3**); M = Cu, A = TfO (**4**)) by coordination or displacement of the weakly coordinated ligands. **1**–**3** are obtained as air- and moisture-stable white solids while **4** slowly

oxidizes to the copper(II) derivative. Their elemental analysis and physical and spectroscopic properties are in accordance with the proposed stoichiometry. Their IR spectra show, among others, the ν(N–H) stretching absorptions in the range 3230–3430 cm^{-1}. Their $^{31}P\{^1H\}$ NMR spectra at room temperature show a singlet at 32.9 (**1**) or -11.7 ppm (**4**) or a multiplet at -2.6 ppm (**2** and **3**) that splits into two doublets centered at -3.6 ppm on cooling to 223 K, as expected for the presence of equivalent phosphorus bonded to a silver atom $[J(^{109}Ag–P) = 574; J(^{107}Ag–P) = 502$ Hz]. The presence of TfO in **1**, **2** and **4** is confirmed by the presence of a single resonance in their ^{19}F NMR while in their ^1H NMR spectra, apart from the resonances arising from the aromatic protons, the signal corresponding to the aminic protons appears at ~4.6 (**1**), 5.14 (**2** and **3**) or ~4.9 ppm (**4**). Their mass spectra are also in accordance with the proposed stoichiometry (see Experimental section).

Single crystals of **2** were obtained in order to determine its crystal structure, but, unfortunately, serious disorder of the nitrogen atoms of the ligands precluded satisfactory refinement. It was however clear that the PNH_2 molecules are acting as monodentate P-bonded to the silver center instead of as bidentate ligands as had been previously suggested.[12c]

One could expect that the same reactions carried out with equimolecular amounts of the starting materials would lead to the homodinuclear $[M(PNH_2)]_2^{2+}$ cations, but in the case of gold this reaction results in the mononuclear $[Au(PNH_2)(tht)]^+$ complex previously described.[12a] Thus, in order to obtain the gold(I) dimer an alternative synthetic pathway was investigated by reacting $[AuCl(PNH_2)]$ with $AgClO_4$ (1:1) in acetone; this surprisingly results in the formation of $[Au(PN=CMe_2)]_2(ClO_4)_2$ (**5**) instead of the expected product. This is an interesting result that implies an unusual condensation process between the amine group of the ligand and an acetone molecule at room temperature. The analytical data and physical and spectroscopic properties agree with this formulation (see Experimental section). The absorptions corresponding to the N–H bonds of

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Table 1 Bond lengths [Å] and angles [°] for compound **5**

Au–N#1	2.093(3)	P–C(11)	1.822(3)
Au–P	2.2482(9)	N–C(7)	1.295(5)
Au–Au#1	2.8396(3)	N–C(6)	1.448(4)
P–C(21)	1.813(3)	C(1)–C(6)	1.395(5)
P–C(1)	1.818(3)	C(1)–C(2)	1.396(5)
N#1–Au–P	172.93(8)	C(7)–N–Au#1	122.0(2)
N#1–Au–Au#1	90.74(7)	C(6)–N–Au#1	117.9(2)
P–Au–Au#1	94.72(2)	C(6)–C(1)–C(2)	118.5(3)
C(21)–P–C(1)	106.36(15)	C(6)–C(1)–P	120.4(2)
C(21)–P–C(11)	106.60(15)	C(2)–C(1)–P	121.0(3)
C(1)–P–C(11)	107.05(15)	C(16)–C(11)–P	122.1(3)
C(21)–P–Au	117.11(11)	C(12)–C(11)–P	118.2(3)
C(1)–P–Au	112.41(11)	C(26)–C(21)–P	120.3(3)
C(11)–P–Au	106.77(11)	C(22)–C(21)–P	119.6(2)
C(7)–N–C(6)	119.8(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$.

the PNH$_2$ are not observed in its IR spectrum, while its ^{31}P{^{1}H} NMR shows a unique resonance at 20.2 ppm. Furthermore, the ^{1}H NMR spectrum of **5** displays (apart from the signals of the aromatic protons) a broad signal at 2.06 ppm corresponding to the methyl groups instead of any resonance due to aminic protons.

Single crystals of **5** were obtained by slow diffusion of diethyl ether into a chloroform solution of the complex and its crystal structure was determined by X-ray analysis in order to confirm this formulation. The cation of compound **5** (Fig. 1, Table 1)
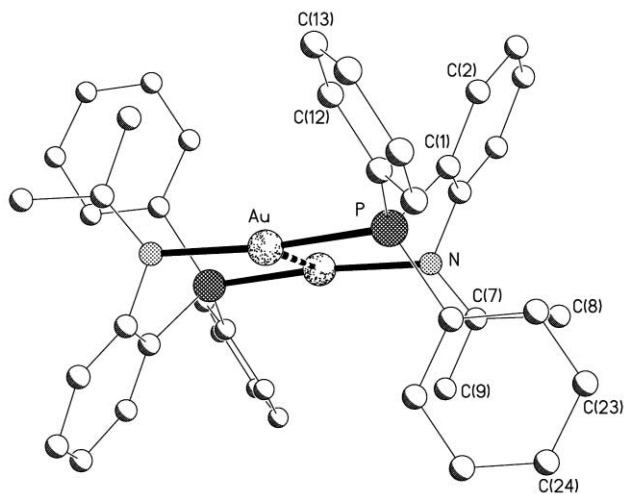

Fig. 1 Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Radii are arbitrary.

possesses an inversion center. The observed distortion from linear geometry associated with the presence of gold · · · gold contacts (N#1–Au–P 172.93(8)°, Au–Au#1 2.8396(3) Å) is well known in dinuclear derivatives of this type. The gold · · · gold interaction is shorter than that observed between the two gold(I) centres in [Au(C$_6$F$_5$)$_2${PN(AuPPh$_3$)$_2$}]ClO$_4$[12h] (2.9749(3) Å) and much shorter than that between gold centres of different molecules in [Au{(±)amp}][12b] (3.1709(5) Å) ((±)amp = (±)-(2-aminophenyl)methylphenylphosphine). Similar Au–P distances to those found in **5** (2.2482(9) Å) have been found in the derivatives [Au(SC$_4$H$_8$)(PNH$_2$)]ClO$_4$[12a] (2.261(2) Å), [Au(C$_6$-F$_5$)$_2${PN(AuPPh$_3$)$_2$}]ClO$_4$ for the Au(I)–P bonds (2.2395(9), 2.2505(9) Å)[12h] or in [AuI(adp)][12b] (2.260(4) Å) (adp = (2-aminophenyl)diphenylphosphine) and [Au{(±)amp}][12b] (2.262(2), 2.256(2) Å). The Au–N#1 distance (2.093(3) Å) is longer than that found in [AuCl$_3$(Hpm)][14] (Hpm = 2-pyridylmethanol) (2.021(9) Å). Finally, a possible C–H · · · O hydrogen bond is found, involving an H · · · O distance of 2.48 Å (see Table 2).

In order to avoid the condensation process that takes place when the reaction of AgClO$_4$ and [AuCl(PNH$_2$)] (1:1) is carried out in acetone, we tested other possible solvents in which the reaction could progress as desired, concluding that the best results were obtained in a mixture of toluene/dichloromethane, from which the complex [Au(PNH$_2$)]$_2$(ClO$_4$)$_2$ (**6**) was finally isolated as a pure compound. The related silver and copper species [M(PNH$_2$)]$_2$A$_2$ (M = Ag, A = TfO (**7**), ClO$_4$ (**8**); M = Cu, A = TfO (**9**)) were more easily synthesized by treatment of the free ligand with equimolecular amounts of AgTfO, AgClO$_4$, or [Cu(NCMe)$_4$]TfO. An alternative synthetic procedure for these three latter complexes consists of the treatment of the mononuclear products **2**–**4** with the same silver(I) or copper(I) salts in a 1:1 molar ratio (see Scheme 1). Complexes **6**–**8** are obtained as white air- and moisture-stable solids, while the copper(I) center in **9** slowly oxidizes to copper(II). Their analytical, physical and spectroscopic data are in accordance with the proposed stoichiometry and they presumably present a head to tail disposition of the ligands as commonly observed in homo-dinuclear complexes containing asymmetric bridging ligands.[15] Their IR spectra display ν(N–H) stretching absorptions in the range 3202–3300 cm^{-1} and their ^{31}P{^{1}H} NMR spectra at room temperature are similar to those registered for the mononuclear derivatives **1**–**4**, although in this case the broad signal observed for the silver compounds **7** and **8** at room temperature is not completely split on cooling. The ^{19}F NMR spectra of the trifluoromethylsulfonate derivatives display the single resonance at −78.25 ppm corresponding to the anion. The resonances due to the aminic protons appear in the ^{1}H NMR spectra at 4.94 (**6**), 5.67 (**7**) and (**8**) or 5.1 ppm (**9**).

Once the homodinuclear complexes **6**–**9** had been prepared, we were interested in synthesizing the mixed Au–Ag, Au–Cu and Ag–Cu dinuclear derivatives in order to analyze their relative stabilities, structural differences and optical properties compared to the homodinuclear species **6**–**9**. Thus, when **6** reacts with AgTfO or [Cu(NCMe)$_4$]BF$_4$ (1:1) or [Au(tht)$_2$]TfO reacts with equimolecular amounts of **2** or **4**, the heterodinuclear complexes [AuM(PNH$_2$)$_2$](TfO)$_2$ (M = Ag (**10**); M = Cu (**11**)) are obtained, where the gold(I) centres are expected to be coordinated through the phosphorus atoms as shown in Scheme 1; this implies an isomerization process when the starting material is [Au(tht)$_2$]TfO, similar to that described by us with other asymmetric ligands.[16] In contrast, reaction of [Ag(PNH$_2$)$_2$]TfO (**2**) with one equivalent of [Cu(NCMe)$_4$]TfO or reaction of [Cu(PNH$_2$)$_2$]TfO (**4**) with AgTfO in a 1:1 molar ratio produces a mixture of the homodinuclear derivatives **7** and **9**, as can be observed in solution by ^{31}P{^{1}H} NMR at 223 K, and as also previously observed with the asymmetric bidentate ligand PPh$_2$CH$_2$SPh.[16] Complexes **10** and **11** were obtained as white solids soluble in acetone and chlorinated solvents and insoluble in diethyl ether and hexane. The ν(N–H) stretching absorptions appear in their IR spectra at 3300 cm^{-1} and their ^{31}P{^{1}H} NMR spectra display a singlet at 31.1 (**10**) or 29.5 ppm (**11**) confirming a head to head disposition of the ligands with the gold atom bonded to the phosphorus centers. The ^{1}H NMR spectra of **10** and **11** show, besides the signals due to the aromatic hydrogens, a singlet corresponding to the aminic protons at 5.18 (**10**) or 5.47 ppm (**11**).

The crystal structure of **10** was determined by X-ray diffraction from single crystals obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. The cation is shown in Fig. 2, with a selection of bond lengths and angles in Table 3. Complex **10** cystallizes together with two half molecules of dichloromethane, which are disordered. The cation consists of a dinuclear mixed-metal unit with the PPh$_2$C$_6$H$_4$NH$_2$ ligands bridging both metals. The gold atom is linearly coordinated to the two phosphorus atoms of the ligands with Au–P distances of 2.325(3) and 2.332(3) Å. These values are similar to those found in bis(phosphine)gold compounds such as [Au(PR$_3$)$_2$]$^+$ (PR$_3$ = PPh$_2$Me, 2.316(4) Å; PCy$_3$,

Table 2 Hydrogen bonds [Å and °]

Compound 5 D–H · · · A	d(D–H)	d(H · · · A)	d(D · · · A)	<(DHA)
C(26)–H(26) · · · O(1)#1	0.95	2.48	3.299(5)	144.2

Compound 12 D–H · · · A	d(D–H)	d(H · · · A)	d(D · · · A)	<(DHA)
N(1)–H(01) · · · O(1)	0.83(2)	2.27(3)	2.997(6)	146(5)
N(1)–H(02) · · · N(2)	0.83(2)	2.64(4)	3.274(7)	134(4)
N(2)–H(03) · · · N(3)	0.83(2)	2.54(4)	3.195(7)	137(5)
N(2)–H(04) · · · O(2)	0.83(2)	2.11(3)	2.920(6)	163(5)
N(3)–H(05) · · · N(1)	0.83(2)	2.51(4)	3.193(6)	141(5)
N(3)–H(06) · · · O(1)	0.83(2)	2.53(4)	3.161(6)	134(5)
N(1)–H(02) · · · Au	0.83(2)	3.13(5)	3.366(4)	99(4)
N(2)–H(03) · · · Au	0.83(2)	2.91(5)	3.278(5)	109(4)
N(3)–H(05) · · · Au	0.83(2)	2.99(5)	3.426(5)	115(4)

Table 3 Selected bond lengths [Å] and angles [°] for compound 10

Au–P(2)	2.325(3)	P(1)–C(6)	1.826(10)
Au–P(1)	2.332(3)	P(1)–C(21)	1.854(11)
Au–Ag	2.9931(12)	P(2)–C(51)	1.833(12)
Ag–N(2)	2.244(9)	P(2)–C(12)	1.836(11)
Ag–N(1)	2.262(9)	P(2)–C(41)	1.842(11)
P(1)–C(31)	1.823(12)		
P(2)–Au–P(1)	167.90(10)	C(6)–P(1)–Au	109.8(3)
P(2)–Au–Ag	95.09(7)	C(21)–P(1)–Au	108.4(4)
P(1)–Au–Ag	94.91(7)	C(51)–P(2)–Au	113.8(4)
N(2)–Ag–N(1)	175.2(3)	C(12)–P(2)–Au	114.5(3)
N(2)–Ag–Au	86.8(2)	C(41)–P(2)–Au	107.6(3)
N(1)–Ag–Au	88.4(2)	C(1)–N(1)–Ag	119.4(6)
C(31)–P(1)–Au	116.7(4)	C(11)–N(2)–Ag	117.0(6)

2.321(2) Å[17–18] although these values are slightly longer than those in gold complexes with heterodifunctional ligands such as [Au(PPh₂CH₂SPh)₂]ClO₄ (2.306(2) and 2.308(2) Å)[16] or

[AuAg(PPh₂CH₂SPh)₂](TfO)₂ (2.3044(11) and 2.3103(11) Å)[3] or [AuAg(PPh₂py)₂](ClO₄)₂ (2.296(2) and 2.297(2) Å).[15b] The silver center is linearly coordinated to two nitrogen atoms with an angle N–Ag–N of 175.2(3)°. The Ag–N bond distances, 2.244(9) and 2.262(9) Å, are longer than those found in other linear silver complexes bonded to amine groups such as [Ag(Ph₂C=NH)₂]BF₄ (2.113(2) Å)[19] and smaller than those with pyridine groups such as [AuAg(PPh₂py)₂](ClO₄)₂ (2.289(8) and 2.310(9) Å),[15b] although in this compound the silver also makes covalent bonds to the perchlorate oxygens. The silver atom also shows weak interactions with the oxygen atoms of the triflate groups, Ag–O2 2.918, Ag–O3 2.821, Ag–O1# 2.765 Å, (# −x + 1, −y + 2, −z + 1). The Ag · · · Au distance in 10 is 2.9931(12) Å and can be considered as a bonding interaction, similar to those found in other heteronuclear complexes such as [AuAg-(PPh₂CH₂SPh)₂](TfO)₂ (2.9314(5) Å)[16] or [Ag(μ-dppm)₂{Au-(mes)₂}₂]ClO₄·3CH₂Cl₂ (2.944(2) and 2.946(2) Å; dppm = bis-(diphenylphosphino)methane; mes = mesityl)[20] or [(AuPPh₃)₂-
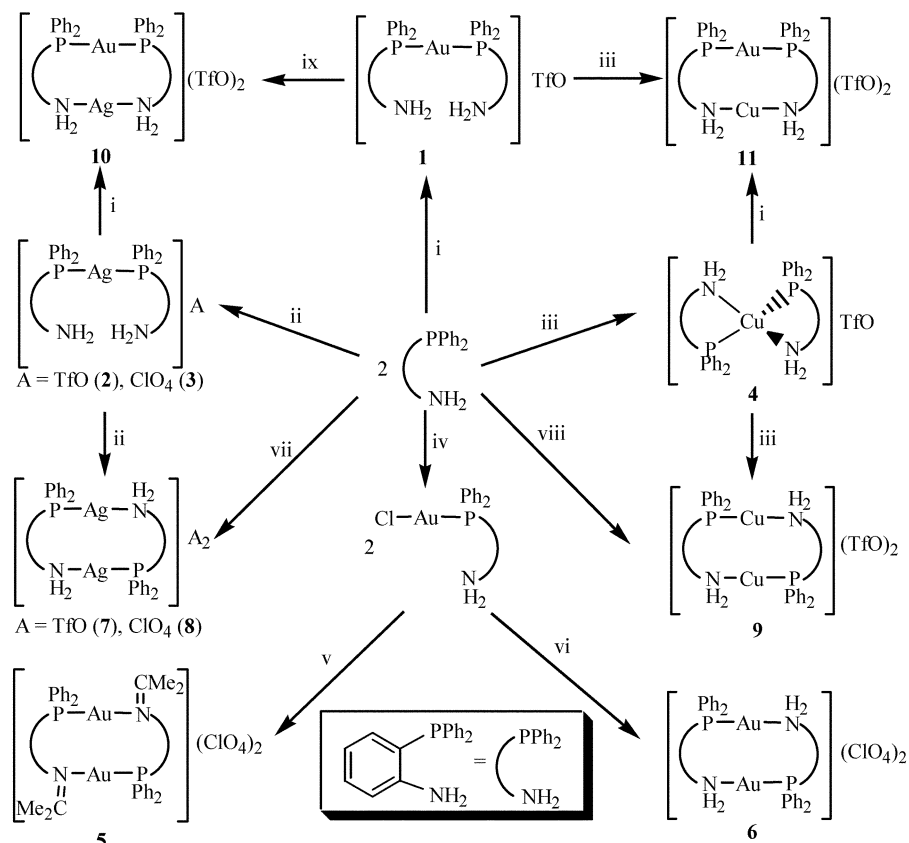
Scheme 1 i) [Au(tht)₂]TfO; ii) AgA; iii) [Cu(NCMe)₄]TfO; iv) 2 [AuCl(tht)]; v) 2 AgClO₄ in acetone; vi) 2 AgClO₄ in CH₂Cl₂/toluene (1/1); vii) 2 AgA; viii) 2 [Cu(NCMe)₄]TfO; ix) AgTfO.

{μ-C(PPh₃)}(C₅H₄N){μ-Ag(O₂NO)(OClO₃)}] (2.926(1) and 3.006(1) Å)[21] or slightly longer than those in [AuAg(PPh₂-py)₂](ClO₄)₂ (2.820(1) Å).[15b] There is one short N–H ··· O hydrogen bond[N(2)–H(2b) ··· O(4#) (# x, 1 + y, z) of 2.283 Å.

As mentioned above, the small number of compounds of 2-(diphenylphosphino)aniline with group 11 metals reported to date were supposed to be linear for gold(I) or tetrahedral for copper or silver, so we tried to prepare new species in which the geometry could be different. Therefore, we treated PNH₂ with the same starting materials as before in a 3:1 molar ratio, a reaction that led to the tris(phosphine) complexes [M(PNH₂)₃]A (M = Au, A = TfO (**12**); M = Ag, A = ClO₄ (**13**); M = Cu, A = TfO (**14**)) (see Scheme 2). They were obtained as stable white solids, except for the copper(I) derivative **14** that is slowly oxidized to copper(II) with atmospheric oxygen. Complexes **12**–**14** are soluble in chlorinated solvents and acetone and insoluble in diethyl ether and hexane and they behave as 1 : 1 electrolytes (see Experimental section). Their IR spectra show the characteristic absorptions of the N–H bonds at ~3325 cm⁻¹ and also those corresponding to the anions at ~1100 (vs, br) and 623 cm⁻¹ (m) for ClO₄⁻[22] or at ~1260 (vs, br), 1153 (br), 1101 (br) and 692 cm⁻¹ (m) for TfO⁻.[23] In the ³¹P{¹H} NMR spectra of **12**–**14** a unique broad signal is observed at 26.0 (**12**), −3.6 (**13**) or −9.1 ppm (**14**) at room temperature that is sharpened for **12** and **14** and splits into two doublets centered at −3.5 ppm for the silver derivative **13** [$J(^{109}\text{Ag–P}) = 365$; $J(^{107}\text{Ag–P}) = 320$ Hz] when they are registered at 223 K. Their ¹H NMR spectra display, besides the resonances corresponding to the aromatic protons, a broad signal due to the aminic hydrogens at 4.74 (**12**), 4.72 (**13**) or 4.65 ppm (**14**) that appears as a singlet on cooling.
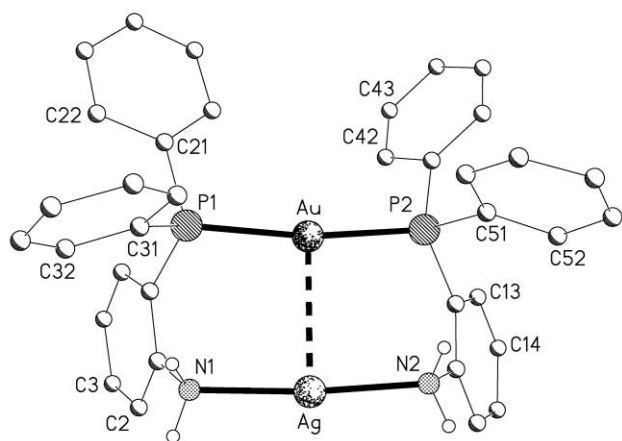
Table 4 Selected bond lengths [Å] and angles [°] for **12**

Au–P(1)	2.3688(12)	N(1)–C(6)	1.383(6)
Au–P(3)	2.3694(13)	N(2)–C(36)	1.394(6)
Au–P(2)	2.3738(12)	N(3)–C(82)	1.388(6)
P(1)–Au–P(3)	120.10(4)	C(41)–P(2)–Au	116.53(15)
P(1)–Au–P(2)	120.43(4)	C(81)–P(3)–Au	114.11(15)
P(3)–Au–P(2)	119.34(4)	C(71)–P(3)–Au	117.93(14)
C(1)–P(1)–Au	113.29(14)	C(61)–P(3)–Au	108.85(15)
C(11)–P(1)–Au	110.37(14)	N(1)–C(6)–C(5)	119.0(5)
C(21)–P(1)–Au	117.59(14)	N(1)–C(6)–C(1)	121.5(4)
C(51)–P(2)–Au	109.35(15)	C(35)–C(36)–N(2)	119.6(4)
C(31)–P(2)–Au	113.47(14)	N(2)–C(36)–C(31)	121.7(4)

Finally, the crystal structure of the tricoordinated gold(I) compound **12** was determined by X-ray diffraction methods from single crystals obtained by slow diffusion of hexane into a solution of **12** in dichloromethane. Compound **12** (Fig. 3, Table 4) crystallizes with one dichloromethane molecule. It exhibits trigonal geometry at the gold centre (P–Au–P angles from 119.34(4) to 120.43(4)°). The metal atom is essentially coplanar with the donor atoms P(1), P(2) and P(3). Au–P distances are very similar and range from 2.3688(12) to 2.3738(12) Å. These values are in the range of those observed in [Au-(PPh₃)₃]⁺ (three independent investigations (2.345–2.408 Å)[24–26] or [Au(dppf)(PPh₃)]ClO₄ (2.343(2)–2.409(2) Å).[27] Within the

Fig. 2 Molecular structure of the cation in **10**. Hydrogen atoms (except NH) are omitted for clarity. Radii are arbitrary.
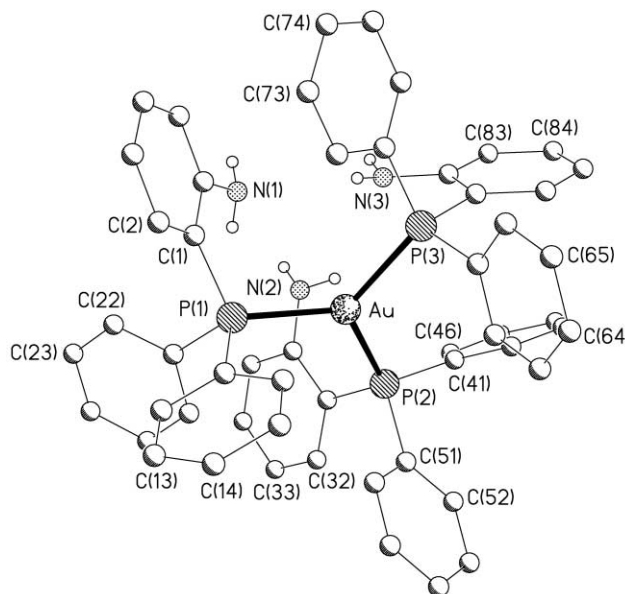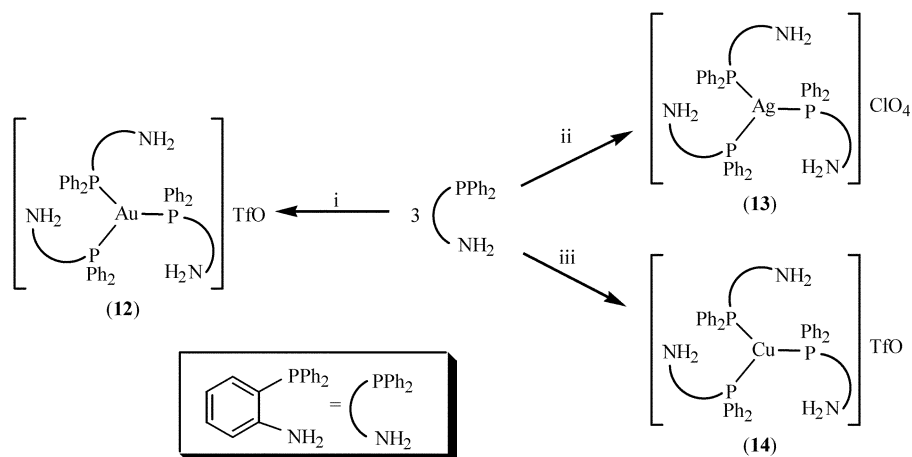

Fig. 3 Molecular structure of the cation in **12**. Hydrogen atoms (except NH) are omitted for clarity. Radii are arbitrary.

Scheme 2 i) [Au(tht)₂]TfO; ii) AgClO₄; iii) [Cu(NCMe)₄]TfO.

asymmetric unit there are two short N–H $\cdots$ O hydrogen bonds (N1–H01 $\cdots$ O1 and N2–H04 $\cdots$ O2); several other borderline interactions with H $\cdots$ X (X = N or O) *ca.* 2.5 Å could be interpreted as hydrogen bonds, and there are additionally some short N–H $\cdots$ Au contacts with H $\cdots$ Au distances of *ca.* 3 Å (Table 2), although the N–H $\cdots$ Au angles are around 100°.

The study of luminescent gold(I) compounds has received great attention and developed rapidly in the last years. Particularly interesting are the multimetallic systems that show metal–metal interactions, because the study of their photophysical and photochemical properties, apart from the fundamental interest, has potential applications in synthesis, energy conversion and pharmacology.[28] The luminescence in gold(I) derivatives is usually: a) related to the presence of metal–metal interactions, b) conditioned by the ligands in internal transitions or in charge transfers, or c) related to a trigonal planar geometry around the gold center. Thus, we have registered the excitation and emission spectra of the gold products described here, which could present such optical properties.

All the spectra recorded in solution show a common feature: a broad emission band at high energy in the range 429–441 nm (excitation: 382–384 nm) that can be assigned to ligand transitions probably located in the π orbitals of the rings. High energy values of intraligand transitions have been reported in related systems[29] and the solution spectrum of the ligand shows an emission at similar values of energy. Thus, the emission spectra of solutions of the dinuclear gold(I) species $[AuM(PNH_2)_2]^{2+}$ (M = Au (**6**), Ag (**10**), Cu (**11**)) show this emission at 441 (**6**), 430 (**10**) or 431 nm (**11**). Nevertheless, a more detailed analysis of these spectra reveals the presence of a second transition that appears as a shoulder in the emission spectrum of the homonuclear gold derivative **6** (see Fig. 4) at
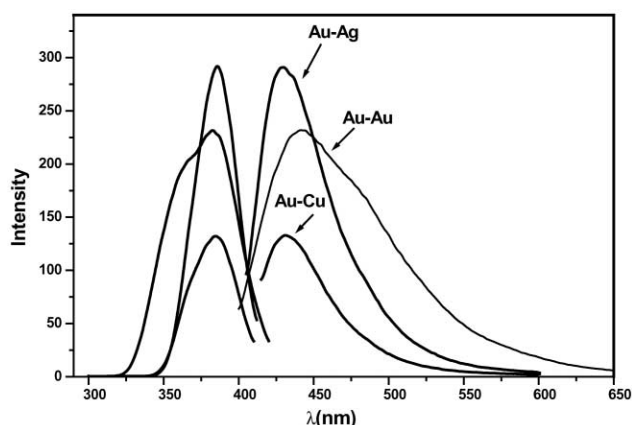

Fig. 4 Excitation and emission spectra of complexes **6**, **10** and **11** in solution at room temperature.

~500 nm (excitation: ~350 nm). The absence of this transition in the other dinuclear complexes allows us to assign tentatively its origin in the interactions between the gold(I) centres. Besides, similar values have also been reported for other dinuclear gold(I) derivatives[30] and assigned as phosphorescence from a triplet excited state. In contrast, these complexes are only very weakly luminescent in the solid state.

It has been shown[31] that tricoordination around a d[10] ion in phosphino complexes produces a reduction of the HOMO–LUMO gap that allows the appearance of luminescent transitions. Thus, the experimental studies of this type of complex in the solid state show emissions ranging between 481 and 533 nm and they are assigned to a phosphorescent emission. In the case of complex **12**, when the excitation and emission spectra are recorded at room temperature only a transition at 440 nm assigned to the ligand is observed, but when the temperature is lowered to 77 K an additional band appears in the emission

spectrum at 500 nm, a value that is in accordance with a phosphorescent transition in the metal promoted by the tricoordination. When the spectrum is recorded in acetone solution only the band corresponding to the intraligand transitions is observed. In the cases of the silver and copper derivatives only a weak luminescence of the ligand is observed either in solution or in the solid state, a fact that could be interpreted as possible tetracoordination around the metal centers.

Experimental

Reagents

AgClO$_4$ and AgTfO were purchased from Aldrich and used as received. The compounds PNH$_2$,[32] [Au(tht)$_2$]TfO,[33] [Cu-(NCMe)$_4$]TfO,[34] [AuCl(PNH$_2$)][12a] were prepared by literature methods.

Caution! perchlorate salts with organic cations may be explosive.

General procedure

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5×10^{-4} M acetone solutions with a Jenway 4010 conductimeter. C, H, N, S analyses were carried out with a Perkin-Elmer 240C microanalyser. Mass spectra were recorded on a VG Autospec using the LSIMS techniques and nitrobenzyl alcohol as the matrix and on a HP59987 A electrospray. ^{1}H, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker ARX 300 in CDCl$_3$ or hexadeuteroacetone (HDA) solutions. Chemical shifts are quoted relative to SiMe$_4$ (^{1}H, external), CFCl$_3$ (^{19}F, external) and H$_3$PO$_4$ (85%) (^{31}P, external). Excitation and emission spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer. Acetone for photophysics was distilled over potassium permanganate and degassed before use. All the experiments were carried out under nitrogen atmosphere using Schlenk techniques and at room temperature.

Synthesis of the complexes

[Au(PNH$_2$)$_2$]TfO (1). To a dichloromethane solution (20 mL) of [Au(tht)$_2$]TfO (0.25 mmol, 0.13 g) was added PNH$_2$ (0.5 mmol; 0.14 g) and after 15 min of stirring the solvent was evaporated to *ca.* 5 mL. Addition of diethyl ether (20 mL) led to precipitation of complex **1** as a white solid. Yield: 80%. Mass spectrum: [M]$^+$ at m/z = 751 (100%). Anal. Calcd. for: C$_{37}$H$_{32}$AuF$_3$N$_2$O$_3$P$_2$S (**1**): C, 49.35; H, 3.6; N, 3.1; S, 3.55. Found: C, 49.5; H, 3.4; N, 3.25; S, 3.6%. ^{31}P{^{1}H} NMR (CDCl$_3$), δ: 32.9 (s). ^{19}F NMR (CDCl$_3$), δ: −78.25 (s). ^{1}H NMR (CDCl$_3$), δ: 6.49–7.61 [m, 28H, aromatic protons], ~4.6 [m, 4H, NH$_2$]. Λ_M = 72 Ω^{-1} cm^2 mol^{-1}.

[Ag(PNH$_2$)$_2$]A (A = TfO (2), ClO$_4$ (3)). To a solution of 0.25 mmol of AgA (A = TfO, 0.06 g; A = ClO$_4$, 0.05 g) in 20 mL of diethyl ether was added PNH$_2$ (0.5 mmol; 0.14 g) and a white precipitate immediately began to form. After 2 h of stirring the precipitation was complete and the white solid was then filtered off. Yield: 80 (**2**), 94% (**3**). Mass spectra: [M]$^+$ at m/z = 661 (100%, **2** and **3**). Anal. Calcd. for: C$_{37}$H$_{32}$AgF$_3$N$_2$O$_3$P$_2$S (**2**): C, 54.75; H, 3.95; N, 3.45; S, 3.95. Found: C, 54.5; H, 3.95; N, 3.45; S, 3.95%. C$_{36}$H$_{32}$AgClN$_2$O$_4$P$_2$ (**3**): C, 56.75; H, 4.25; N, 3.7. Found: C, 56.45; H, 4.45; N, 3.45%. ^{31}P{^{1}H} NMR (HDA), 298 K, δ: (**2**) −2.7 (m); (**3**) −2.6 (m); 223 K, δ: (**2**) −3.6 [J(^{109}Ag–P) = 574; J(^{107}Ag–P) = 502 Hz]; (**3**) −3.6 [J(^{109}Ag–P) = 574; J(^{107}Ag–P) = 502 Hz]. ^{19}F NMR (HDA), δ: (**2**) −78.25 (s). ^{1}H NMR (HDA), 223 K, δ: (**2**) 6.56–7.60 [m, 28H, aromatic protons], 5.62 [s, 4H, NH$_2$]; (**3**) 6.74–7.61 [m, 28H, aromatic protons], 5.14 [s, 4H, NH$_2$]. Λ_M = 68 (**2**); 78 Ω^{-1} cm^2 mol^{-1} (**3**).

[Cu(PNH₂)₂]TfO (4). To an acetonitrile solution (20 mL) of [Cu(NCMe)₄]TfO (0.25 mmol; 0.09 g) was added PNH₂ (0.5 mmol; 0.14 g) and after 15 min of stirring the solvent was evaporated to *ca.* 5 mL. Addition of diethyl ether (20 mL) led to precipitation of complex **4** as a white solid. Yield: 61%. Mass spectrum: [M]⁺ at *m/z* = 617 (100%). Anal. Calcd. for: $C_{37}H_{32}CuF_3N_2O_3P_2S$ (**4**): C, 57.95; H, 4.2; N, 3.65; S, 4.2. Found: C, 57.75; H, 4.05; N, 3.95; S, 4.3%. ³¹P{¹H} NMR (CDCl₃), δ: −11.7 (s). ¹⁹F NMR (CDCl₃), δ: −78.25 (s). ¹H NMR (CDCl₃), δ: 7.13–7.4 [m, 28H, aromatic protons], ~4.9 [m, 4H, NH₂]. Λ_M = 70 Ω⁻¹ cm² mol⁻¹.

[Au(PN=CMe₂)]₂(ClO₄)₂ (5). To a solution of AgClO₄ (0.25 mmol; 0.05 g) in acetone was added [AuCl(PNH₂)] (0.25 mmol; 0.13 g). After 3 h of stirring the AgCl formed was filtered off and the resulting solution was concentrated in vacuum. Addition of 20 mL of diethyl ether led to precipitation of **5** as a white solid. Yield: 86%. Anal. Calcd. for: $C_{42}H_{40}Au_2Cl_2N_2O_8P_2$ (**5**): C, 41.1; H, 3.3; N, 2.3. Found: C, 40.9; H, 3.35; N, 2.3%. ³¹P{¹H} NMR (HDA), δ: 20.5 (s). ¹H NMR (HDA), δ: 7.13–7.93 [m, 28H, aromatic protons], 2.06 [m, 12H, Me]. Λ_M = 125 Ω⁻¹ cm² mol⁻¹.

[Au(PNH₂)]₂(ClO₄)₂ (6). To a solution of AgClO₄ (0.25 mmol; 0.05 g) in dichloromethane/toluene (1/1) was added [AuCl(PNH₂)] (0.25 mmol; 0.13 g). After 3 h of stirring the AgCl formed was filtered off and the resulting solution was concentrated in vacuum. Addition of 20 mL of diethyl ether led to precipitation of **6** as a white solid. Yield: 95%. Anal. Calcd. for: $C_{36}H_{32}Au_2Cl_2N_2O_8P_2$ (**6**): C, 37.7; H, 2.8; N, 2.45. Found: C, 37.75; H, 2.9; N, 2.5%. ³¹P{¹H} NMR (CDCl₃), δ: 17.1 (s). ¹H NMR (CDCl₃), δ: 6.45–7.72 [m, 28H, aromatic protons], 4.94 [s, 4H, NH₂]. Λ_M = 120 Ω⁻¹ cm² mol⁻¹.

[Ag(PNH₂)]₂A₂ (A = TfO (7), ClO₄ (8)). *Method 1.* To a diethyl ether solution (20 mL) of 0.5 mmol of AgA (A = TfO, 0.13 g; A = ClO₄, 0.14 g) was added PNH₂ (0.5 mmol, 0.14 g) and a white precipitate immediately started to form. After 2 h of stirring at room temperature the precipitation was complete; complexes **7** and **8** were obtained as white solids that were then filtered off. Yield: 72 (**7**), 97% (**8**).

Method 2. To a solution of 0.2 mmol of AgA (A = TfO, 0.05 g; A = ClO₄, 0.04 g) in acetone was added 0.2 mmol of **2** (0.16 g) (**7**) or **3** (0.15 g) (**8**). After 15 min of stirring the solution was concentrated in vacuum and addition of 20 mL of diethyl ether led to the precipitation of complexes **7** and **8** as white solids. Yield: 70 (**7**), 85% (**8**). Mass spectra: [M˙A]⁺ at *m/z* = 919 (6%, **7**); 869 (6%, **8**). Anal. Calcd. for: $C_{38}H_{32}Ag_2F_6N_2O_6P_2S_2$ (**7**): C, 42.7; H, 3.0; N, 2.6; S, 6.0. Found: C, 42.6; H, 3.15; N, 2.35; S, 6.05%. $C_{36}H_{32}Ag_2Cl_2N_2O_8P_2$ (**8**): C, 44.6; H, 2.35; N, 2.9. Found: C, 44.35; H, 3.25; N, 3.1%. ³¹P{¹H} NMR (HDA): 298 K, δ: (**7**) −0.8 (m); (**8**) −0.8 (m); 223 K, δ: (**7**) −2.10 (broad doublet); (**8**) −2.4 (broad doublet). ¹⁹F NMR (HDA), δ: (**7**) −78.25 (s). ¹H NMR (HDA), 223 K, δ: (**7**) 6.71–7.66 [m, 28H, aromatic protons], 5.67 [s, 4H, NH₂]; (**8**) 6.72–7.64 [m, 28H, aromatic protons], 5.68 [s, 4H, NH₂]. Λ_M = 128 (**7**); 117 Ω⁻¹ cm² mol⁻¹ (**8**).

[Cu(PNH₂)]₂(TfO)₂ (9). *Method 1.* To an acetonitrile solution (20 mL) of [Cu(NCMe)₄]TfO (0.5 mmol; 0.19 g) was added PNH₂ (0.5 mmol; 0.14 g). After 15 min of stirring at room temperature the solvent was evaporated to *ca.* 5 mL and addition of diethyl ether (20 mL) led to precipitation of **9** as a white solid. Yield: 70%.

Method 2. To a solution of [Cu(NCMe)₄]TfO (0.2 mmol, 0.07 g) in acetonitrile was added 0.2 mmol of **4** (0.15 g). After 15 min of stirring the solution was concentrated in vacuum and addition of 20 mL of diethyl ether led to the precipitation of complex **9** as a white solid. Yield: 65%. Anal. Calcd. for:

$C_{38}H_{32}Cu_2F_6N_2O_6P_2S_2$ (**9**): C, 46.6; H, 3.3; N, 2.85; S, 6.55. Found: C, 46.7; H, 3.25; N, 2.75; S, 6.7%. ³¹P{¹H} NMR (CDCl₃) δ: −10.8 (s). ¹⁹F NMR (CDCl₃), δ: −78.25 (s). ¹H NMR (CDCl₃), δ: 6.68–7.47 [m, 28H, aromatic protons], ~5.1 [m, 4H, NH₂]. Λ_M = 124 Ω⁻¹ cm² mol⁻¹.

[AuM(PNH₂)₂](TfO)₂ (M = Ag (10), Cu (11)). *Method 1.* A dichloromethane solution of complex **1** (0.2 mmol, 0.18 g) was added to a solution of 0.2 mmol of AgTfO (0.05 g) in diethyl ether (**10**) or [Cu(NCMe)₄]TfO (0.07 g) in acetonitrile (**11**). After 15 min of stirring at room temperature the solvent was evaporated to *ca.* 5 mL and addition of diethyl ether (20 mL) led to precipitation of complexes **10** or **11** as white solids. Yield: 83 (**10**); 86% (**11**).

Method 2. To a solution of [Au(tht)₂]TfO (0.2 mmol, 0.10 g) in 20 mL of dichloromethane was added 0.2 mmol of **4** (0.15 g) or **2** (0.16 g). The solution was stirred for 15 min and then concentrated in vacuum. Addition of diethyl ether (20 mL) led to the precipitation of complexes **10** or **11** as white solids. Yield: 90 (**10**); 78% (**11**). Anal. Calcd. for: $C_{38}H_{32}AgAuF_6N_2O_6P_2S_2$ (**10**): C, 39.45; H, 2.8; N, 2.4; S, 5.55. Found: C, 39.55; H, 2.65; N, 2.45; S, 5.65%. $C_{38}H_{32}AgCuF_6N_2O_6P_2S_2$ (**11**): C, 41.0; H, 2.9; N, 2.5; S, 5.75. Found: C, 40.7; H, 2.95; N, 2.85; S, 5.65%. ³¹P{¹H} NMR (CDCl₃): δ: (**10**) 31.1 (s); (**11**) 29.5 (s). ¹⁹F NMR (CDCl₃), δ: (**10** and **11**) −78.25 (s). ¹H NMR (CDCl₃), δ: (**10**) 6.73–7.65 [m, 28H, aromatic protons], 5.18 [s, 4H, NH₂]; (**11**) 6.74–7.59 [m, 28H, aromatic protons], 5.47 [s, 4H, NH₂]. Λ_M = 124 (**10**); 105 Ω⁻¹ cm² mol⁻¹ (**11**).

[Au(PNH₂)₃]ClO₄ (12). To a dichloromethane solution (20 mL) of [Au(tht)₂]ClO₄ (0.2 mmol, 0.10 g) was added PNH₂ (0.6 mmol; 0.17 g) and after 30 min of stirring at room temperature the solvent was evaporated to *ca.* 5 mL. Addition of diethyl ether (20 mL) led to precipitation of complex **12** as a white solid. Yield: 77%. Anal. Calcd. for: $C_{55}H_{48}AuF_3N_3O_3P_3S$ (**12**): C, 56.1; H, 4.1; N, 3.55; S, 2.7. Found: C, 54.8; H, 4.4; N, 3.35; S, 2.6%. ³¹P{¹H} NMR (CDCl₃), 298 K, δ: 26.0 (m); 223 K, δ: 28.8 (s). ¹⁹F NMR (CDCl₃), δ: −78.25 (s). ¹H NMR (CDCl₃), δ: 6.57–7.37 [m, 42H, aromatic protons], 4.74 [m, 6H, NH₂]. Λ_M = 73 Ω⁻¹ cm² mol⁻¹.

[Ag(PNH₂)₃]ClO₄ (13). To a solution of 0.2 mmol of AgClO₄ (0.04 g) in 20 mL of diethyl ether was added PNH₂ (0.6 mmol; 0.17 g); a white precipitate immediately appeared. After 3 h of stirring the precipitation was complete and the white solid was filtered off. Yield: 88%. Anal. Calcd. for: $C_{54}H_{48}AgClN_3O_4P_3$ (**13**): C, 62.4; H, 4.65; N, 4.05. Found: C, 61.7; H, 5.05; N, 3.85%. ³¹P{¹H} NMR (HDA): 298 K, δ: −3.6 (m); 223 K, δ: −3.5 [J(¹⁰⁹Ag–P) = 365; J(¹⁰⁷Ag–P) = 320 Hz]. ¹H NMR (HDA): δ: 6.75–7.51 [m, 42H, aromatic protons], 4.72 [s, 6H, NH₂]. Λ_M = 81 Ω⁻¹ cm² mol⁻¹.

[Cu(PNH₂)₃]TfO (14). To an acetonitrile solution (20 mL) of [Cu(NCMe)₄]TfO (0.2 mmol, 0.07 g) was added PNH₂ (0.6 mmol; 0.17 g) and after 30 min of stirring the solvent was evaporated to *ca.* 5 mL. Addition of diethyl ether (20 mL) led to precipitation of complex **14** as a white solid. Yield: 70%. Anal. Calcd. for: $C_{55}H_{48}CuF_3N_3O_3P_3S$ (**14**): C, 63.25; H, 4.65; N, 4.0; S, 3.05. Found: C, 63.0; H, 4.35; N, 3.75; S, 2.85%. ³¹P{¹H} NMR (CDCl₃), 298 K, δ: −9.1 (m); 223 K, δ: −8.3 (s). ¹⁹F NMR (CDCl₃), δ: −78.25 (s). ¹H NMR (CDCl₃), δ: 6.64–7.31 [m, 42H, aromatic protons], 4.65 [m, 6H, NH₂]. Λ_M = 73 Ω⁻¹ cm² mol⁻¹.

Crystal structure determinations

The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens P4 or Siemens-Smart 1000-CCD (**5**) diffractometers. Data were collected using monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption

Table 5 Details of data collection and structure refinement for complexes **5**, **10** and **12**

Compound	**5**	**10·2×1/2CH₂Cl₂**	**12·CH₂Cl₂**
Chemical formula	$C_{42}H_{40}Au_2Cl_2N_2O_8P_2$	$C_{39}H_{34}AgAuCl_2F_6N_2O_6P_2S_2$	$C_{56}H_{50}AuCl_2F_3N_3O_3P_3S$
Crystal habit	Colourless tablet	Colourless prism	Colourless tablet
Crystal size/mm	$0.18 \times 0.08 \times 0.06$	$0.50 \times 0.30 \times 0.20$	$0.20 \times 0.14 \times 0.14$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.5581(8)	12.027(3)	11.5579(18)
b/Å	11.2666(12)	12.451(3)	12.209(2)
c/Å	11.8309(12)	16.605(4)	20.646(3)
a/°	70.274(3)	76.38(1)	101.310(12)
β/°	78.216(3)	72.23(2)	92.877(14)
γ/°	80.113(3)	87.81(1)	103.841(12)
U/Å³	1044.61(18)	2299.8(10)	27593(7)
Z	1	2	2
D_c/g cm⁻³	1.951	1.794	1.520
M	1227.53	1242.48	1262.83
$F(000)$	592	1212	1264
T/°C	−130	−100	−100
$2\theta_{max}$/°	56	50	50
μ(Mo-Kα)/mm⁻¹	7.274	3.958	2.943
Transmission	0.928–0.708	0.242–0.505	0.681–0.876
No. of reflections measured	14295	9296	11619
No. of unique reflections	5166	7998	9641
R_{int}	0.0436	0.0481	0.0255
$R^a(F > 4\sigma(F))$	0.0251	0.0601	0.0350
$wR^b(F^2$, all refl.)	0.0543	0.1589	0.0665
No. of reflections used	5166	7998	9641
No. of parameters	264	605	662
No. of restraints	65	349	195
S^c	0.990	1.031	0.911
Max. $\Delta\rho$/e Å⁻³	1.716	2.87	0.832

^{a} $R(F) = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$. ^{b} $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. ^{c} $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

corrections were based on ψ-scans (**10**, **12**) or multiple scans (program SADABS (**5**)).[35] The structures were refined on F^2 using the program SHELXL-97.[36] All non-hydrogen atoms were refined anisotropically. H atoms were included using a riding model or rigid methyl groups (exceptions see below). *Special features of refinement*: for all compounds, restraints to light atom U value components and to local ring symmetry were employed to improve the stability of the refinement. The solvent molecules in complex **10** (two half molecules of dichloromethane) are disordered over inversion centres. The aminic hydrogens of compound **12** were located in difference syntheses and refined with fixed U values and restrained N–H distances. Further crystallographic details are given in Table 5.

CCDC reference numbers 176612–176614.

See http://www.rsc.org/suppdata/dt/b1/b110398a/ for crystallographic data in CIF or other electronic format.

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