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From Diphosphane to Diphosphodiide Gold(III) Derivatives of 1,2-Diphosphinobenzene

M. Carmen Blanco,[a] Eduardo J. Fernández,*[a] M. Elena Olmos,[a] Javier Pérez,[a] and Antonio Laguna*[b]

Dedicated to Professor Víctor Riera on the occasion of his 70th birthday

Abstract: Treatment of 1,2-diphosphinobenzene with $[Au(C_6F_5)_3(tht)]$ leads to the diphosphane derivative $[\{Au(C_6F_5)_3\}(1,2\text{-}PH_2C_6H_4PH_2)]$ (**1**), which further reacts with other pentafluorophenylgold(III) reagents in the presence of acetylacetonate as deprotonating agent to afford phosphane–phosphide complexes. The noncyclic $PPN[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)]$ (**2**; PPN = bis(triphenylphosphine)iminium) has been shown to be a useful starting material for the synthesis of higher nuclearity cyclic or noncyclic diphosphide or even diphosphodiide derivatives through similar reactions. The crystal structures of the trinuclear anionic $NBu_4[\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_2Cl\}\{\mu\text{-}Au(C_6F_5)_2\}]$ (**3**) and the hexanuclear $[\{Au(C_6F_5)_3\}(1,2\text{-}PC_6H_4P)\{Au(C_6F_5)_3\}\{\mu\text{-}M(dppe)M\}_2]$ (M = Au (**12**), Ag (**13**)) have been established by X-ray diffraction methods, the last complexes having a bicyclic ring containing three intramolecular interactions between the M^I centres.

Keywords: copper · gold · phosphane ligands · silver

Introduction

The chemistry of phosphido-bridged derivatives of the main group elements[1–3] or transition metals[4–6] has been a matter of interest for various research groups during the last few years. Whereas there is a great number of phosphido complexes with metals mainly of Groups 6[7–12] or 10,[13–20] the chemistry of gold derivatives has experienced less progress in this research field, in spite of the possible catalytic behaviour of di- and polynuclear phosphido-bridged compounds.[21]

Thus, when we started our work in this research field, only a few gold(I) complexes containing PR_2H[22–25] or PR_2^-[23,24,26,27] ligands were known and even less numerous were the species derived from primary phosphines, with the only examples of compounds of the type $[AuX(PRH_2)]$[28] or aurated phosphonium salts[29] reported by Schmidbaur. Only very recently a series of cyclic and noncyclic phosphide complexes derived from secondary phosphines have been reported,[30] as well as some tri- or hexaaurated phosphonium salts.[31] Moreover, in the case of gold(III), its chemistry with both primary or secondary phosphines or their phosphide derivatives was almost nonexistent, with Puddephatt's $[Au_2Me_4(\mu\text{-}PPh_2)_2]$[26] as the only example.

In the last few years our group has reported the synthesis and reactivity of a number of gold(III) phosphino and phosphido derivatives of PPh_2H[32] and we have also recently described a series of cyclic and noncyclic gold(III) phosphine, phosphide and phosphodiide derivatives of the primary phosphine $PPhH_2$.[33]

To increase the nuclearity of the products and to obtain different structural dispositions, we chose the primary diphosphine 1,2-diphosphinobenzene, which contains four hydrogen atoms that could be removed and substituted by a metal atom. Moreover, the *ortho* disposition of the PH_2 groups seemed to be adequate for the incorporation of metal atoms at distances short enough to show metal–metal interactions.

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[a] M. C. Blanco, Dr. E. J. Fernández, M. E. Olmos, J. Pérez
Departamento de Química, Universidad de La Rioja
Grupo de Síntesis Química de La Rioja, UA-CSIC
Obispo Bustamante 3, 26001 Logroño (Spain)
Fax: (+34) 941-299-621
E-mail: eduardo.fernandez@dq.unirioja.es

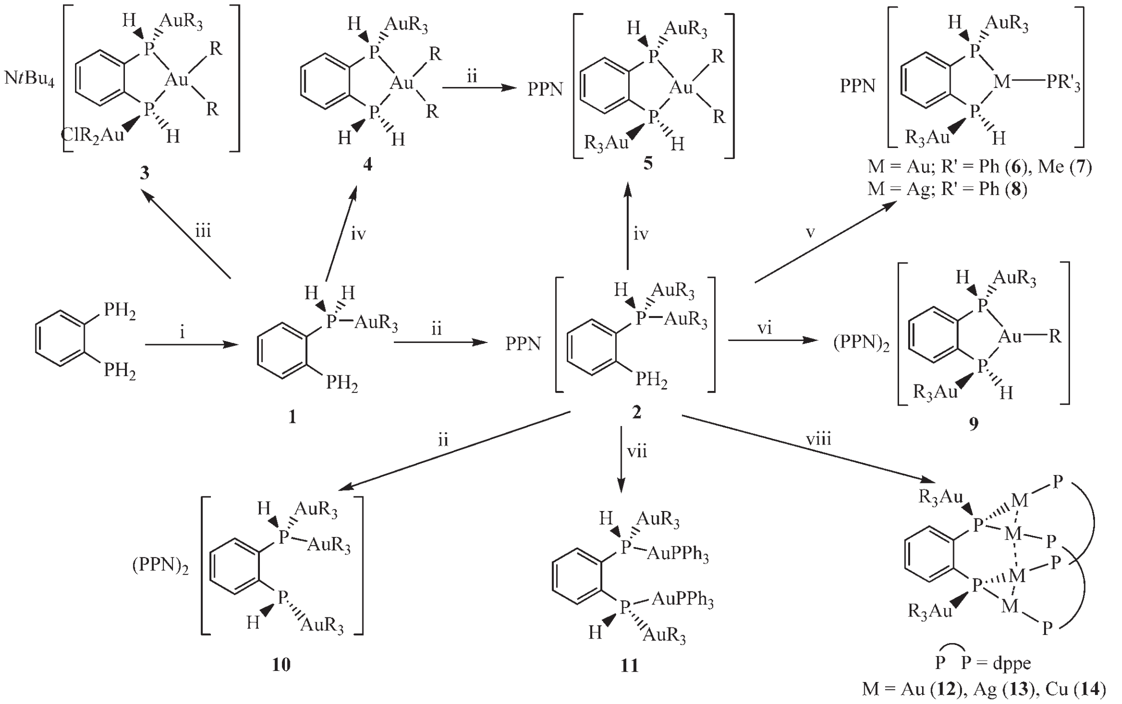
[b] Prof. Dr. A. Laguna
Departamento de Química Inorgánica
Instituto de Ciencia de Materiales de Aragón
Universidad de Zaragoza-CSIC, 50009 Zaragoza (Spain)
Fax: (+34) 976-761-187
E-mail: alaguna@posta.unizar.es

In this paper we describe the synthesis of the diphosphane complex $[\{Au(C_6F_5)_3\}(1,2\text{-}PH_2C_6H_4PH_2)]$ (**1**) and its phosphido derivative $PPN[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)]$ (**2**) (PPN = bis(triphenylphosphine)iminium) and the study of their utility as precursors for the preparation of diphosphides or diphosphodiides of higher nuclearity, that is, from two to six metal atoms.

Abstract in Spanish: *El tratamiento de 1,2-difosfinobenceno con* $[Au(C_6F_5)_3(tht)]$ *conduce a la síntesis del difosfino derivado* $[\{Au(C_6F_5)_3\}(1,2\text{-}PH_2C_6H_4PH_2)]$ *(**1**), que reacciona con otros pentafluorofenil complejos de oro(III) en presencia de acetilacetonato como agente desprotonante conduciendo a la obtención de fosfino-fosfuro complejos. El compuesto* $PPN[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)]$ *(**2**) se ha mostrado como un producto de partida de gran utilidad para la síntesis de difosfuro o incluso difosfodiuro derivados cíclicos o no cíclicos de mayor nuclearidad a través de reacciones similares. Las estructuras cristalinas del complejo trinuclear aniónico* $NBu_4[\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_2Cl\}\{\mu\text{-}Au(C_6F_5)_2\}]$ *(**3**) y de los hexanucleares* $[\{Au(C_6F_5)_3\}(1,2\text{-}PC_6H_4P)\{Au(C_6F_5)_3\}\{\mu\text{-}M(dppe)M\}_2]$ *(M = Au (**12**), Ag (**13**)) se han determinado mediante difracción de rayos X, mostrando cada una de las dos últimas un biclico que contiene tres interacciones intramoleculares entre los centros de* M^I.

Results and Discussion

The 1,2-diphosphinobenzenegold(III) complex $[\{Au(C_6F_5)_3\}(1,2\text{-}PH_2C_6H_4PH_2)]$ (**1**) was prepared by displacement of the weakly coordinated ligand tht (tetrahydrothiophene) from $[Au(C_6F_5)_3(tht)]$ when treated with the free diphosphine in a 1:1 molar ratio (see Scheme 1). Complex **1** was isolated as a moderately air- and moisture-stable white solid, soluble in most common organic solvents and insoluble in *n*-hexane. Its analytical and spectroscopic data are in agreement with the proposed stoichiometry (see Experimental Section) showing the presence of absorptions from a tris(pentafluorophenyl)gold(III) fragment[34] at 1505 (vs), 965 (vs) and 797 cm^{-1} (s, br) and a weak absorption at 2329 cm^{-1}, corresponding to the ν(P–H) stretching band.[35]



Scheme 1. $R = C_6F_5$; i) $[AuR_3(tht)]$; ii) $[AuR_3(tht)]$ + PPN(acac); iii) $[Au(\mu\text{-}Cl)R_2]_2$ + NBu_4(acac); iv) $[AuR_2(acac)]$; v) $[Au(acac)(PPh_3)]$ or $[AuCl(PMe_3)]$ + Tl(acac) or $[Ag(TfO)(PPh_3)]$ + PPN(acac); vi) $[AuR(tht)]$ + PPN(acac); vii) $[\{Au(PPh_3)\}_2(\mu\text{-}Cl)]ClO_4$; viii) $2[(AuCl)_2(dppe)]$ + $4AgClO_4$ + 3PPN(acac) or $2[M_2(dppe)](TfO)_2$ (M = Ag, Cu) + 3PPN(acac).

Its $^{31}P\{^1H\}$ NMR spectrum at 223 K displays two doublets at $\delta = -61.6$ and -125.7 ppm ($^3J(P,P) = 48$ Hz), corresponding to the coordinated and the free phosphorus atoms, respectively. Working with $1,2\text{-}C_6H_4(PH_2)_2$ we have found the information obtained from ^{31}P NMR spectra to be particularly useful, and, consequently, we measured the ^{31}P NMR spectra for some of the complexes described. In the ^{31}P NMR spectrum of complex **1**, each doublet in the $^{31}P\{^1H\}$ NMR spectrum appears as a triplet of doublets as a consequence of the coupling of each phosphorus atom with two hydrogen atoms directly bonded to it. It is worth noting the different magnitude of both J(P,H) coupling constants:

416 Hz for the phosphorus bonded to gold(III) and 214 Hz for the free phosphorus atom.

On the other hand, its ^{19}F NMR spectrum displays the three typical groups of resonances of $Au(C_6F_5)_3$ fragments (see Experimental Section), while in its ^{1}H NMR spectrum at 223 K two doublets centred at 6.08 and 4.10 ppm are observed in addition to the signals due to the aromatic protons. Finally, the mass spectrum of **1** (electrospray in the negative ion mode; ES−) shows the molecular peak at $m/z=839$ (20%) with an experimental isotopic distribution in accordance to the theoretical one.

When complex **1** is treated with a second equivalent of $[Au(C_6F_5)_3(tht)]$ or the previous reaction is carried out in a 2:1 molar ratio in order to incorporate a second gold centre to the molecule, compound **1** is always obtained as the product. By contrast, if **1** is treated with $[Au(C_6F_5)_3(tht)]$ and PPN(acac) (1:1:1), one of the phosphinic hydrogen atoms is replaced by a second tris(pentafluorophenyl)gold(III) moiety, resulting in the formation of the anionic phosphane–phosphide $PPN[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)]$ (**2**), in which both gold centres bind the same phosphorus atom (see Scheme 1), which suggests that the protons bonded to this atom are more acid than those of the free phosphorus. Compound **2** is obtained as a stable white solid that shows a molar conductivity in acetone typical of 1:1 electrolytes.

Its IR spectrum is very similar to that of complex **1**, also showing an absorption at 2318 cm^{-1} corresponding to the ν(P−H) stretching band. The $^{31}P\{^1H\}$ NMR spectrum of **2** at 223 K displays, in addition to the singlet due to the PPN$^+$ ion at $\delta=21.1$ ppm, two doublets at $\delta=-62.3$ and -118.9 ppm ($^3J(P,P)=42$ Hz), that is, at positions very similar to those found in the spectrum of complex **1**; this similarity suggests that both gold(III) centres are bonded to the same phosphorus atom. This supposition is confirmed by the ^{31}P NMR spectrum of **2** in which the signal at lower field appears as a doublet of doublets, while the signal at $\delta=-118.9$ ppm, which corresponds to the free phosphorus atom, shows a triplet of doublets.

The ^{19}F NMR spectrum of **2** confirms the equivalence of both $Au(C_6F_5)_3$ fragments and its ^{1}H NMR spectrum displays, in addition to the signals of the aromatic protons, two doublets centred at $\delta=5.97$ and 3.95 ppm, respectively, with relative intensities 1:2. Finally, in the mass spectrum of **2** (ES−), the peak corresponding to the molecular anion appears at $m/z=1538$ (85%).

From our experience of working with other phosphines, we have found that the dinuclear derivative $[\{Au(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ has led to interesting results on other occasions;[32b,33] therefore we treated **1** with equimolecular amounts of $[\{Au(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ in the presence of one equivalent of $NBu_4(acac)$. Both the acetylacetonate and one of the chlorine atoms act as deprotonating agents in a reaction that proceeds with the breaking of the dinuclear compound and leads to the incorporation of an $Au(C_6F_5)_2Cl$ unit and a bridging $Au(C_6F_5)_2$ fragment; this reaction results in the formation of the trinuclear complex *trans*-$NBu_4[\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_2Cl\}\{\mu\text{-}Au(C_6F_5)_2\}]$ (**3**; see Scheme 1). This new compound was obtained as a white stable solid at room temperature that behaves as a 1:1 electrolyte in acetone.

The analytical and spectroscopic data are in agreement with the proposed stoichiometry for **3**. The IR spectrum shows bands corresponding to the presence of C_6F_5 groups bonded to gold(III), and absorptions at 2338 and 311 cm^{-1} associated to the ν(P−H)[35] and ν(Au−Cl)[36] stretching bands, respectively.

The nonequivalence of both phosphorus atoms is shown in the $^{31}P\{^1H\}$ NMR spectrum, which displays two singlets at $\delta=0.3$ and -9.8 ppm (no $^3J(P,P)$ is observed in this case) that split into doublets in the ^{31}P NMR spectrum ($J(P,H)=392$ and 382 Hz, respectively), indicating that each phosphorus atom is still bonded to one hydrogen atom. The high number of nonequivalent pentafluorophenyl groups bonded to gold(III) in complex **3** makes the ^{19}F NMR spectrum very complicated. Nevertheless, in the region of the spectrum in which the signals from the *para*-fluorine atoms are expected, six triplets with relative intensities 1:1:1:1:2:1, in agreement with the presence of seven C_6F_5 rings, are observed.

The ^{1}H NMR spectrum of **3** again shows two doublets in addition to the signals of the aromatic protons and the resonances due to the NBu_4^+ ion (see Experimental Section). Its mass spectrum (ES−) shows as parent peak that corresponding to the molecular anion at $m/z=1936$.

Finally, by slow diffusion of *n*-hexane into a solution of **3** in chloroform, single-crystals suitable for X-ray diffraction studies were obtained and its crystal structure determined. The anion of complex **3** is shown in Figure 1, with selected bond lengths and angles in Table 1. The anion consists of a central $(1,2\text{-}PHC_6H_4PH)\{\mu\text{-}Au(C_6F_5)_2\}$ fragment, in which the pentafluorophenyl rings are nearly perpendicular to the plane formed by the 1,2-diphosphidobenzenegold(III) unit, with the terminal $Au(C_6F_5)_3$ and $Au(C_6F_5)_2Cl$ moieties located *trans* to each other and bonded to P1 and P2, respectively. The five-membered metallacycle is almost planar, as well

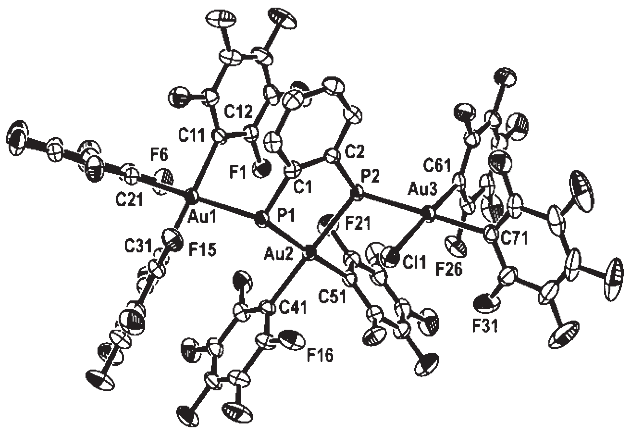


Figure 1. Structure of the anion of complex **3** (30% probability level) with the labelling scheme of the atom positions. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complex **3**.

Au1−C11	2.068(7)	Au2−P2	2.3313(18)
Au1−C21	2.075(7)	Au3−C61	2.030(7)
Au1−C31	2.078(7)	Au3−C71	2.074(7)
Au1−P1	2.3527(17)	Au3−Cl1	2.3245(18)
Au2−C51	2.086(7)	Au3−P2	2.3416(17)
Au2−C41	2.086(7)	P1−C1	1.808(7)
Au2−P1	2.3274(18)	P2−C2	1.816(7)
C11-Au1-C21	89.3(3)	C61-Au3-C71	90.8(2)
C11-Au1-C31	176.9(2)	C61-Au3-Cl1	175.94(19)
C21-Au1-C31	90.1(3)	C71-Au3-Cl1	90.16(18)
C11-Au1-P1	89.73(17)	C61-Au3-P2	93.38(18)
C21-Au1-P1	178.77(18)	C71-Au3-P2	175.18(19)
C31-Au1-P1	90.93(18)	Cl1-Au3-P2	85.88(6)
C51-Au2-C41	90.5(2)	C1-P1-Au2	106.6(2)
C51-Au2-P1	177.12(18)	C1-P1-Au1	109.5(2)
C41-Au2-P1	91.62(18)	Au2-P1-Au1	115.72(7)
C51-Au2-P2	91.79(17)	C2-P2-Au2	107.3(2)
C41-Au2-P2	175.24(17)	C2-P2-Au3	106.7(2)
P1-Au2-P2	86.25(6)	Au2-P2-Au3	112.49(7)

as the environment of the metal atoms, which display the usual square-planar geometry of gold(III) with mean deviations for the best plane of only 0.021 Å for Au1 and Au2 and 0.012 Å for Au3. The participation of Au2 in the metallacycle causes the greatest distortion of the environment of Au^{III}, which is observed in the angle P1-Au2-P2 of 86.25(6)°, as observed in the related bis(pentafluorophenyl)phosphido derivatives $[\{Au(C_6F_5)_2(\mu\text{-}PPh_2)\}_2]$ (79.61(7)°)[32b] or $[\{Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Ag\}_2]$ (89.29(8) and 89.50(8)°).[32c] The Au−C bond lengths range from 2.030(7) to 2.086(7) Å, the shortest corresponding to the C_6F_5 group *trans* to Cl and the longest to those *trans* to P; this result seems to indicate a higher *trans* influence for the phosphorus atom of the phosphide than for the perfluorophenyl groups and even higher if compared to chlorine. The Au−P distances, which lie in the range 2.327(2)–2.353(2) Å, are in general shorter than those found in other noncyclic gold(III) phosphido complexes;[32,33] however, the longest bond is similar to those found in the trinuclear cyclic $[\{Au(C_6F_5)_2(\mu\text{-}PPhH)\}_3]$ (average 2.359 Å).[33] Regarding the Au−Cl distance of 2.3245(18) Å, it is of the same order as those observed in the related compounds $[Au(C_6F_5)_2Cl(o\text{-}PPh_2C_6H_4NH_2)]$ (2.3230(11) Å)[37] or $[Au(C_6F_5)_2Cl\{PPh_2CH(Aupy)PPh_2\}AuCl]$ (2.337(8) Å).[38] The phosphorus atoms of the bridging diphosphido ligand show a regular tetrahedral geometry as expected in the absence of short gold–gold interactions (Au1–Au2 = 3.963; Au2–Au3 = 3.885 Å).

The dinuclear derivative $[\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH_2)\{Au(C_6F_5)_2\}]$ (**4**), which displays a chiral phosphorus atom, has two enantiomers and also contains a bridging bis(pentafluorophenyl)gold(III) fragment, was obtained by reaction of **1** with equimolecular amounts of $[Au(C_6F_5)_2(acac)]$. This reaction takes place with the substitution of one of the hydrogen atoms bonded to the phosphorus atom already coordinated to gold(III), confirming their higher acidity relative to the phosphinic protons of the free phosphorus atoms, as suggested in the synthesis of **2**. It was isolated as a pale yellow solid soluble in most common organic solvents and insoluble in *n*-hexane; the analytical and spectroscopic properties of compound **4** agree with the proposed formulation (see Scheme 1).

The IR spectrum of complex **4** is similar to the one registered for the starting complex **1**, with the ν(P−H) stretching band at 2327 cm^{-1}. The singlets at $\delta = -8.4$ and -32.6 ppm observed in its $^{31}P\{^1H\}$ NMR spectrum split into a doublet and a triplet with *J*(P,H) coupling constants of 434 and 398 Hz, respectively, in the ^{31}P NMR spectrum; these results allow the unequivocal assignment of these signals. The same *J*(P,H) coupling constants can be determined from the ^1H NMR spectrum, in which the phosphinic protons appear as doublets (1:2) centred at $\delta = 6.07$ and 6.46 ppm. The ^{19}F NMR spectrum of **4** in the *para*-fluorine region displays for triplets (1:1:2:1) in agreement with the presence of a $Au(C_6F_5)_3$ and a *cis*-$Au(C_6F_5)_2$ units in the molecule. Finally, its mass spectrum (atmospheric pressure chemical ionization in the negative mode; APCI−) shows the molecular peak at $m/z = 1369$ as parent peak.

When the same reaction as before was carried out with **2** instead of **1** as the starting material, a similar process was observed, although in this case the concomitant migration of one tris(pentafluorophenyl)gold(III) unit from one phosphorus atom to the other was also observed, resulting in the isolation of $PPN[\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_3\}\{\mu\text{-}Au(C_6F_5)_2\}]$ (**5**) as pale yellow stable solid. Complex **5** can also be synthesized by treatment of **4** with $[Au(C_6F_5)_3(tht)]$ and PPN(acac) (1:1:1) as shown in Scheme 1. It is obtained as a pale yellow solid with a molar conductivity in acetone solution typical for 1:1 electrolytes.

The equivalence of both phosphorus atoms is confirmed by the $^{31}P\{^1H\}$ NMR spectrum, in which, in addition to the signal due to the PPN^+ ion, a singlet at $\delta = -21.0$ ppm is observed. It is worth noting that both phosphorus atoms of **5**, as well as those in complex **3**, are chiral and one could expect the presence of resonances of the two pairs of diasteromers. Nevertheless, in both cases only one of these pairs is detected in their NMR spectra; this result could indicate a high stereoselectivity of the process that could be due to the high steric demand of the great number of pentafluorophenyl groups. In the case of complex **3**, its crystal structure confirms the presence of the *trans* isomer in the solid state, which allows us to tentatively assign the same disposition for complex **5**.

With regard to the ^{19}F NMR spectrum of **5**, it shows the groups of signals corresponding to two equivalent $Au(C_6F_5)_3$ groups and *cis*-$Au(C_6F_5)_2$ unit, while in the ^1H NMR spectrum a doublet located at $\delta = 6.11$ ppm (*J*(P,H) = 363 Hz) is observed for the hydrogen atoms bonded to phosphorus atoms.

Complex **2** has been shown to be a precursor for the preparation of other trinuclear diphosphides of the type $PPN[\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_3\}\{\mu\text{-}M(PR_3)\}]$ (M = Au, R = Ph (**6**), Me (**7**); M = Ag, R = Ph (**8**)) by treatment with equimolecular amounts of the requisite gold(I) or silver(I) starting material in the presence of acetylacetonate (see Scheme 1). It is worth mentioning that, as in the case of **5**, the migration of one tris(pentafluorophenyl)gold(III) unit occurs during the reaction, and that the new metallic centre binds both phosphorus atoms acquiring a trigonal planar environment, which leads to a more symmetric product than the starting material. They are isolated as yellow, air- and moisture-stable solids that behave as conductors in acetone and with analytical and spectroscopic properties in agreement with the proposed stoichiometry.

The IR spectra still show weak bands at 2327 cm^{-1}, indicating the presence of P–H bonds, as well as the absorptions characteristic of $Au(C_6F_5)_3$ fragments and PPN^+. The $^{31}P\{^1H\}$ NMR spectrum of **6** shows an AX_2 system at $\delta = 45.5$ (t) and −11.9 ppm (d), as expected for a molecule with a trigonal planar gold(I) centre. In the case of complex **7**, the environment seems to be less symmetric, showing a doublet of doublets instead of a triplet for the phosphorus atom of the PR_3 and broader resonances for the phosphorus atom of the diphosphide ligand in its $^{31}P\{^1H\}$ NMR spectrum. Finally, the spectrum of the silver derivative even when registered at low temperature displays broad signals than cannot be completely resolved as a consequence of the additional coupling with ^{107}Ag and ^{109}Ag.

Complexes **6--8** have nearly identical ^{19}F NMR spectra and a similar pattern for the hydrogen atoms bonded to phosphorus in their ^1H NMR spectra, displaying signals that could be described as two doublets located at the same chemical shift, $\delta = 5.52$ (**6**), 5.48 (**7**), and 4.29 ppm (**8**), but with different J(P,H) coupling constants. Finally, the mass spectra of **6** and **7** show the peak assigned to the molecular anion at $m/z = 1995$ (25) and 1809 (85 %), respectively.

A neutral $Au(C_6F_5)$ fragment was incorporated when **2** was treated with $[Au(C_6F_5)(tht)]$ and PPN(acac) (1:1:1), a reaction that takes place in a similar way to the previous ones, and lead to the formation of the mixed Au^I/Au^{III} diphosphide $(PPN)_2[\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_3\}\{\mu\text{-}Au(C_6F_5)\}]$ (**9**). This new complex was isolated as a pale yellow solid soluble in most common organic solvents and in acetone it shows a molar conductivity characteristic of 2:1 electrolytes.

The IR spectrum of complex **9** is very similar to that registered for the starting complex **2**, with the presence of a new strong absorption at 962 cm^{-1}, indicating the presence of a C_6F_5 group bonded to gold(I), as the main difference. The presence of two singlets at similar chemical shifts ($\delta =$ −34.6 and −38.3 ppm) in the $^{31}P\{^1H\}$ NMR spectrum of **9** seems to indicate that both isomers (*trans* and *cis*) are present now, probably due to a lower estereoselectivity caused by the lower steric demand of the $Au(C_6F_5)$ fragment. The high number of nonequivalent fluorine atoms and the presence of isomers makes the ^{19}F NMR spectrum of **9** very complicated, although resonances due to $Au(C_6F_5)_3$ and $Au(C_6F_5)$ units can be seen. The signals of the phosphidic protons cannot be detected in the ^1H NMR spectrum, probably because of the high number of aromatic hydrogen atoms (64). Nevertheless, the peak corresponding to the molecular anion is located at $m/z = 1900$ (100 %) in its mass spectrum (ES−).

Complex **2** also reacts with $[Au(C_6F_5)_3(tht)]$ and PPN(acac) (1:1:1) to incorporate a third $Au(C_6F_5)_3$ fragment resulting in the synthesis of the trinuclear dianionic complex $(PPN)_2[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_3\}]$ (**10**), which is less symmetric than compounds **5**–**9** and has nonequivalent phosphorus atoms (see Scheme 1). It was isolated as a yellow solid with similar physical properties to **9** and with analytical and spectroscopic data in agreement with the proposed formulation.

The IR and ^{19}F NMR spectra resemble those of the starting product, while in the $^{31}P\{^1H\}$ NMR spectrum the substitution of a hydrogen atom by a tris(pentafluorophenyl)gold(III) is evident with the displacement of the signal corresponding to the free phosphorus atom from $\delta = -118.9$ (**2**) to −58.0 ppm (**10**). Finally, as in complex **9**, in the ^1H NMR spectrum only signals corresponding to aromatic hydrogen atoms can be seen.

In an attempt to increase the number of metallic centres we treated complex **2** with an equimolecular amount of $[\{Au(PPh_3)\}_2(\mu\text{-}Cl)]ClO_4$, a reaction in which the bridging chlorine atom acts as deprotonating agent leading to the formation of the tetranuclear neutral diphosphido complex $[\{Au(C_6F_5)_3\}\{Au(PPh_3)\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_3\}\{Au(PPh_3)\}]$ (**11**; see Scheme 1). As in other cases, the migration of one $Au(C_6F_5)_3$ groups from one phosphorus atom to the other leads to a more symmetric product. Compound **11** is obtained as a yellow, stable solid soluble in most common organic solvents and insoluble in *n*-hexane.

The IR spectrum of complex **11** has absorptions at 1505 (vs), 967 (vs), 793 (br, m) and 534 cm^{-1}, characteristic of the presence of $Au(C_6F_5)_3$ (first three bands) and $Au(PPh_3)$ (last band) units. The equivalence of both phosphorus atoms of the diphosphide ligand is confirmed in the $^{31}P\{^1H\}$ NMR spectrum, which displays an AX system with the doublets centred at $\delta = 44.7$ (*P*Ph$_3$) and −37.1 ppm (*P*H) and $^2J(P,P) = 303$ Hz. The latter signal splits into a doublet of doublets ($J(P,H) = 364$ Hz) when the coupling with ^1H is allowed. The ^{19}F NMR spectrum of **11** resembles that registered for complex **2**, while in its ^1H NMR spectrum a unique doublet at $\delta = \approx 6.3$ ppm is observed. In addition, the molecular peak is observed at $m/z = 2693$ (35 %) in its mass spectrum (Fast atom bombardment in the negation ion mode; FAB−).

Although only the crystal structure of **3** has been determined and it does not show metal–metal interactions, complexes **2** and **4**–**11** presumably do not have such interactions either. In our experience of phosphido gold complexes,[32,33] in the absence of other factors that get the metals closer (such as additional bridging ligands), the Au-P-M angles in phosphido derivatives tend to be wider than 109.5° and the metals tend to be far from each other. To increase the number of metallic centres and to get the metals closer we chose the dinuclear gold(I) derivative $[(AuCl)_2(dppe)]$, which contains a bridging ligand, as starting material. As the chlorine atoms of this complex are not basic enough to extract the hydrogen atoms of $PPN[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)]$ (**2**), we treated it with $[(AuCl)_2(dppe)]$ and $AgClO_4$ in a 1:2:4 molar ratio and in the presence of three equivalents of PPN(acac). This reaction lead to the synthesis of the hexanuclear diphosphodiide derivative $[\{Au(C_6F_5)_3\}(1,2\text{-}PC_6H_4P)\{Au(C_6F_5)_3\}\{\mu\text{-}Au(dppe)Au\}_2]$ (**12**). Similarly, the mixed Au^{III}/M^{I} complexes $[\{Au(C_6F_5)_3\}(1,2\text{-}PC_6H_4P)\{Au(C_6F_5)_3\}\{\mu\text{-}M(dppe)M\}_2]$ (M = Ag(**13**), Cu(**14**)) were prepared. Compounds **12**–**14** are yellow, air- and moisture-stable solids, soluble in acetone, chlorinated solvents and diethyl ether and insoluble in *n*-hexane; in addition they are non-conducting in acetone.

The IR and ^{19}F NMR spectra again display the typical signals of tris(pentafluorophenyl)gold(III) derivatives. The $^{31}P\{^1H\}$ NMR spectra confirm the presence of the diphosphine ligands, showing a new resonance (usually observed as a multiplet even at low temperature) at $\delta = \approx 35$ (**12**), ≈ 2 (**13**) and ≈ 6 ppm (**14**), while the phosphorus atoms of the diphosphodiide ligand appear at higher field: $\delta = -13.6$ (**12**), $\approx$-80 (**13**) and $\approx$-50 ppm (**14**). Also the ^1H NMR spectra of **12**–**14** confirm the presence of dppe in the molecule, displaying a multiplet for the methylenic protons at $\delta = \approx 2.7$ ppm.

Finally, by slow diffusion of *n*-hexane into a solution of **12** or **13** in chloroform, single crystals suitable for X-ray diffraction studies were obtained. X-ray analysis of these crystals allowed us to establish their structures, which are nearly identical (Figures 2 (**12**) and 3 (**13**)). Selected bond lengths and angles are collected in Tables 2 and 3. Each molecule consists of a 16-membered bicycle formed by the *ipso* carbon atoms and both phosphorus atoms of the 1,2-diphosphodiidebenzene ligand, the two M(dppe)M units (M = Au (**12**), Ag (**13**)), with each phosphorus atom of the diphosphodiide also bonded to a tris(pentafluorophenyl)gold(III) unit.

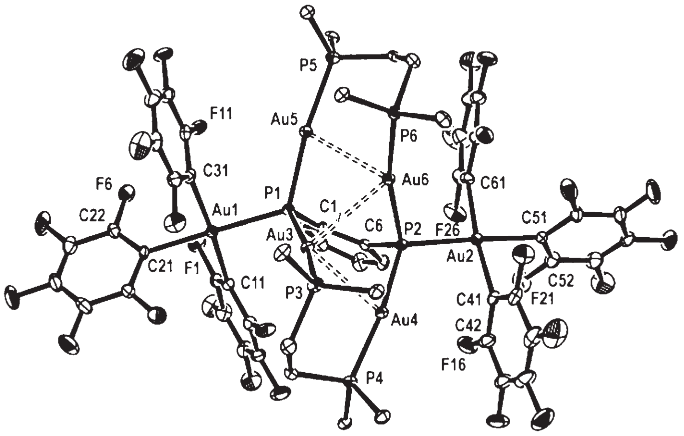


Figure 2. Molecular structure of complex **12** (30 % probability level) with the labelling scheme of the atom positions. Hydrogen atoms have been omitted for clarity.

The gold(III) centres have a regular square-planar geometry with mean deviations for the best plane of only 0.083 Å and 0.043 Å for Au(1) and Au(2), respectively, and with Au–C bond lengths ranging from 2.058(10) to 2.104(8) Å (**12**) and from 1.932(19) to 2.096(16) Å (**13**), the longest ones corresponding to a carbon atom *trans* to P as observed in the crystals structure of **3**. The Au^{III}–P distances (2.375(2) and 2.385(2) Å (**12**) and 2.375(4) and 2.382(4) Å (**13**)) are slightly longer than those described for complex **3** and closer to those found in diphenylphosphidogold(III) derivatives.[32]

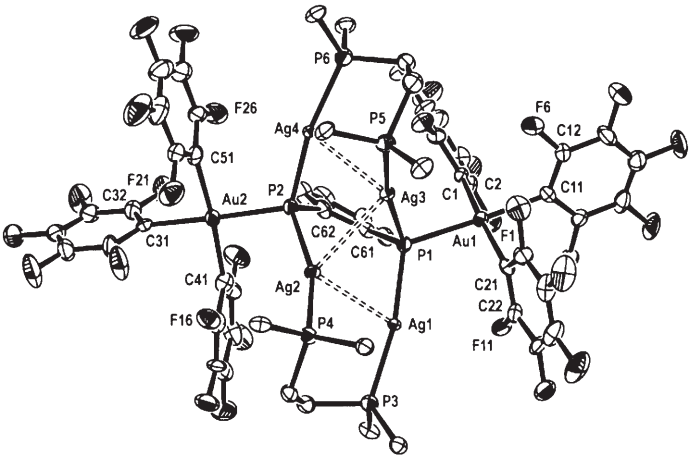


Figure 3. . Molecular structure of complex **13** (30 % probability level) with the labelling scheme of the atom positions. Hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for complex **12**.

Au1–C31	2.064(9)	Au1–C11	2.080(9)
Au1–C21	2.104(8)	Au1–P1	2.375(2)
Au2–C41	2.058(10)	Au2–C51	2.085(9)
Au2–C61	2.086(9)	Au2–P2	2.385(2)
Au3–P3	2.325(2)	Au3–P1	2.340(2)
Au4–P4	2.302(2)	Au4–P2	2.335(2)
Au5–P5	2.299(2)	Au5–P1	2.328(2)
Au6–P6	2.306(2)	Au6–P2	2.323(2)
Au3–Au4	2.9385(5)	Au3–Au6	3.1105(5)
Au5–Au6	3.0273(5)		
C31-Au1-C11	174.1(3)	C31-Au1-C21	87.8(3)
C11-Au1-C21	88.2(3)	C31-Au1-P1	89.5(2)
C11-Au1-P1	95.0(2)	C21-Au1-P1	173.4(3)
C41-Au2-C51	88.4(4)	C41-Au2-C61	173.7(4)
C51-Au2-C61	86.2(3)	C41-Au2-P2	88.9(3)
C51-Au2-P2	177.3(3)	C61-Au2-P2	96.6(2)
P3-Au3-P1	170.92(8)	P4-Au4-P2	170.21(8)
P5-Au5-P1	170.74(9)	P6-Au6-P2	166.32(8)
Au4-Au3-Au6	78.566(12)	Au5-Au6-Au3	76.342(12)
C1-P1-Au5	103.3(3)	C1-P1-Au3	114.1(3)
Au5-P1-Au3	108.70(9)	C1-P1-Au1	109.3(3)
Au5-P1-Au1	119.08(9)	Au3-P1-Au1	102.86(9)
C6-P2-Au6	111.8(3)	C6-P2-Au4	104.1(3)
Au6-P2-Au4	110.71(10)	C6-P2-Au2	106.2(3)
Au6-P2-Au2	106.69(9)	Au4-P2-Au2	117.31(9)

The M^{I} centres are linearly coordinated to two phosphorus atoms (one from dppe and one from $1,2\text{-}PC_6H_4P$) with M^{I}–P bond lengths ranging from 2.299(2) to 2.340(2) Å for **12** and from 2.362(5) to 2.413(5) Å for **13**; these bond

Table 3. Selected bond lengths [Å] and angles [°] for complex **13**.

Au1−C21	2.069(17)	Au1−C1	2.084(16)
Au1−C11	2.096(16)	Au1−P1	2.375(4)
Au2−C41	1.932(19)	Au2−C31	2.026(17)
Au2−C51	2.051(19)	Au2−P2	2.382(4)
Ag1−P1	2.363(5)	Ag1−P3	2.367(5)
Ag1−Ag2	2.9822(16)	Ag2−P4	2.370(5)
Ag2−P2	2.378(5)	Ag2−Ag3	3.0514(16)
Ag3−P5	2.405(5)	Ag3−P1	2.413(5)
Ag3−Ag4	2.9215(15)	Ag4−P6	2.362(5)
Ag4−P2	2.375(5)	P1−C62	1.858(16)
P2−C61	1.791(18)		
C21-Au1-C1	174.7(5)	C21-Au1-C11	88.8(5)
C1-Au1-C11	87.5(5)	C21-Au1-P1	89.4(4)
C1-Au1-P1	94.6(4)	C11-Au1-P1	174.1(4)
C41-Au2-C31	87.5(7)	C41-Au2-C51	173.4(6)
C31-Au2-C51	89.7(6)	C41-Au2-P2	94.2(5)
C31-Au2-P2	177.7(4)	C51-Au2-P2	88.8(4)
P1-Ag1-P3	168.61(16)	P1-Ag1-Ag2	71.23(11)
P3-Ag1-Ag2	101.59(12)	P4-Ag2-P2	160.74(16)
P4-Ag2-Ag1	85.22(12)	P2-Ag2-Ag1	113.25(12)
P4-Ag2-Ag3	118.33(12)	P2-Ag2-Ag3	71.64(11)
Ag1-Ag2-Ag3	82.44(4)	P5-Ag3-P1	168.90(16)
P5-Ag3-Ag4	81.64(12)	P1-Ag3-Ag4	108.59(11)
P5-Ag3-Ag2	117.12(12)	P1-Ag3-Ag2	69.35(11)
Ag4-Ag3-Ag2	83.92(4)	P6-Ag4-P2	166.29(17)
P6-Ag4-Ag3	98.83(12)	P2-Ag4-Ag3	74.18(11)

lengths compare well with those obtained for the related complexes PPN[$\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2M$] (M = Au, Ag),[32a] [$\{Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Ag\}_2$] or [$Au(C_6F_5)_3(\mu\text{-}PPh_2)M(PPh_3)$] (M = Au, Ag)[32c] in the range 2.3025(17)–2.319(2) Å for Au and 2.383(2)–2.4172(10) Å for Ag.

Finally, an important feature in these structures is the presence of intramolecular Au···Au (**12**) or Ag···Ag (**13**) interactions (the latter interaction is observed much less frequently) of 2.9385(5), 3.0273(5) and 3.1105(5) Å in **12** or 2.9215(15), 2.9822(16) and 3.0514(16) Å in **13**. These contacts are probably the responsible of the deviation from the linearity observed in the environment of M^I, which shows P-M-P angles of 166.32(8)–170.92(8)° (**12**) or 160.74(16)–168.90(16)° (**13**). These interactions together with the formation of rings may be the cause of the distortion also found in the tetrahedral environment of the phosphorus atoms, with M-P−M bond angles between 102.86(9) and 119.08(9)° in **12** and between 98.79(17) and 116.16(18)° in **13**.

Experimental Section

Instrumentation: Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer FT-IR Spectrum 1000 spectrophotometer by using Nujol mulls between polyethylene sheets. Conductivities were measured in acetone at a concentration of $\approx 5\times10^{-4}$ M with a Jenway 4010 conductimeter. C, H, N analyses were carried out with a Perkin–Elmer 240C microanalyser. $^{31}P\{^1H\}$, ^{31}P, ^{19}F and ^1H NMR spectra were recorded on a Bruker ARX 300 in $CDCl_3$. Chemical shifts are quoted relative to H_3PO_4 ($^{31}P\{^1H\}$ and ^{31}P), $CFCl_3$ (^{19}F, external) and $SiMe_4$ (^1H, external). Mass spectra were recorded on a HP-5989B Mass Spectrometer API-Electrospray with interface 59987 A or on a VG Autospec by using FAB techniques and nitrobenzyl alcohol as matrix. MS data given in text are not always performed by FAB.

Solvent and reagent pretreatment: Dichloromethane and hexane were distilled from CaH_2 and diethyl ether from sodium, under nitrogen atmosphere. 1,2-Diphosphinobenzene was purchased from Strem, [$Ag(TfO)(PPh_3)$] was obtained by reaction of equimolecular amounts of [$AgCl(PPh_3)$][39] and AgTfO, [M_2dppe]$(TfO)_2$ (M = Ag, Cu) were prepared by treatment of AgTfO or [$Cu(NCMe)_4$]TfO with dppe (2:1), [$Cu(NCMe)_4$]TfO was prepared as described[40] by using triflic acid instead of tetrafluoroboric acid.

Synthesis of [$\{Au(C_6F_5)_3\}(1,2\text{-}PH_2C_6H_4PH_2)$] (1): $o\text{-}C_6H_4(PH_2)_2$ (0.2 mmol, 0.03 mL) was added to a solution of [$Au(C_6F_5)_3(tht)$][34] (0.2 mmol, 0.157 g) in diethyl ether (20 mL). After 1 h of stirring, the solution was concentrated to about 5 mL and by addition of hexane (20 mL) complex **1** was precipitated as a white solid. Yield: 92 %; ^{31}P NMR ($CDCl_3$): $\delta = -61.6$ (td, $J(P,P) = 48$, $J(P,H) = 416$ Hz, 1P; PH_2AuR_3), −125.7 ppm (td, $J(P,P) = 48$, J(P,H) = 214 Hz, 1P; PH_2); ^{19}F NMR ($CDCl_3$): $\delta = -120.1$ (m, 4F; o-F), −154.7 (t, $^3J(F_p,F_m) = 20.5$ Hz, 2F; p-F), −159.6 (m, 4F; m-F), −121.8 (m, 2F; o-F), −156.0 (t, $^3J(F_p,F_m) = 20.5$ Hz, 1F; p-F), −160.7 ppm (m, 2F; m-F); ^1H NMR ($CDCl_3$): $\delta = 7.75$–7.35 (m, 4H; Ph), 6.08 (d, $J(P,H) = 416$ Hz, 2H; PH_2AuR_3), 4.10 (d, $J(P,H) = 214$ Hz, 2H; PH_2); elemental analysis calcd (%) for $C_{24}H_8AuF_{15}P_2$: C 34.31, H 0.96; found: C 34.90, H 0.94; $\Lambda_M = 35\ \Omega^{-1}cm^2mol^{-1}$.

Synthesis of PPN[$\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)$] (2): [$Au(C_6F_5)_3(tht)$] (0.2 mmol, 0.157 g) and PPN(acac)[41] (0.2 mmol, 0.127 g) were added to a freshly prepared solution of **1** (0.2 mmol, 0.168 g) in dichloromethane (20 mL). After stirring for 1 h, partial evaporation of the solvent and addition of hexane led to the precipitation of **2** as a white solid. Yield: 88 %; ^{31}P NMR ($CDCl_3$): $\delta = 21.1$ (s, 2P; PPN), −62.3 (dd, $J(P,P) = 42$, $J(P,H) = 357$ Hz, 1P; $PH(AuR_3)_2$), −118.9 ppm (td, $J(P,P) = 42$, $J(P,H) = 210$ Hz, 1P; PH_2); ^{19}F NMR ($CDCl_3$): $\delta = -120.2$ (m, 4F; o-F), −158.1 (t, $^3J(F_p,F_m) = 20.5$ Hz, 2F; p-F), −161.7 (m, 4F; m-F), −120.6 (m, 4F; o-F), −158.1 (t, $^3J(F_p,F_m) = 20.5$ Hz, 2F; p-F), −161.7 (m, 4F; m-F), −121.3 (m, 4F; o-F), −158.4 (t,$^3J(F_p,F_m) = 20.6$ Hz, 2F; p-F), −161.7 ppm (m, 4F; m-F); ^1H NMR ($CDCl_3$): $\delta = 7.68$–7.39 (m, 34H; Ph), 5.97 (d, $J(P,H) = 357$ Hz, 1H; $PH(AuR_3)_2$), 3.95 ppm (d,$J(P,H) = 210$ Hz, 2H; PH_2); elemental analysis calcd (%) for $C_{78}H_{37}Au_2F_{30}NP_4$: C 45.13, H 1.80, N 0.67; found: C 45.62, H 1.79, N 0.66; $\Lambda_M = 86\ \Omega^{-1}cm^2mol^{-1}$.

Synthesis of *trans*-NBu_4[$\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_2Cl\}\{\mu\text{-}Au(C_6F_5)_2\}$] (3): [$Au(C_6F_5)_2(\mu\text{-}Cl)$]$_2$[42] (0.2 mmol, 0.227 g) and NBu_4(acac)[41] (0.2 mmol, 0.070 g) were added to a freshly prepared solution of **1** (0.2 mmol, 0.168 g) in dichloromethane (20 mL). After stirring for 1 h, partial evaporation of the solvent and addition of hexane led to the precipitation of **3** as a white solid. Yield: 60 %; ^{31}P NMR ($CDCl_3$): $\delta = 0.3$ (d, $J(P,H) = 392$ Hz, 1P; $PHAuR_3$), −9.8 ppm (d, $J(P,H) = 382$ Hz, 1P; $PHAuR_2Cl$); ^{19}F NMR ($CDCl_3$): $\delta = -118.1$ (m, 1F; o-F), −119.8 (m, 1F; o-F), −155.8 (t, $^3J(F_p,F_m) = 19.6$ Hz, 1F; p-F), −158.9 (m, 1F; m-F), −159.4 (m, 1F; m-F), −118.5 (m, 2F; o-F), −122.3 (m, 2F; o-F), −156.6 (t, $^3J(F_p,F_m) = 19.5$ Hz, 2F; p-F), −161.0 (m, 4F; m-F), −120.2 (m, 2F; o-F), −153.8 (t, $^3J(F_p,F_m) = 19.9$ Hz, 1F; p-F), −161.0 (m, 2F; m-F), −121.2 (m, 1F; o-F), −123.5 (m, 1F; o-F), −155.8 (t, $^3J(F_p,F_m) = 19.9$ Hz, 1F; p-F), −160.0 (m, 1F; m-F), −163.4 (m, 1F; m-F), −121.9 (m, 2F; o-F), −156.1 (t, $^3J(F_p,F_m) = 19.5$ Hz, 1F; p-F), −161.8 (m, 2F; m-F), −123.0 (m, 2F; o-F), −157.6 (t, $^3J(F_p,F_m) = 19.5$ Hz, 1F; p-F), −161.8 ppm (m, 2F; m-F); ^1H NMR ($CDCl_3$): $\delta = 7.99$–7.20 (m, 4H; Ph), 6.08 (d, $J(P,H) = 392$ Hz, 1H; $PHAuR_3$), 5.80 (d, $J(P,H) = 382$ Hz, 1H; $PHAuR_2Cl$), 3.12 (m, 8H; CH_2), 1.61 (m, 8H; CH_2), 1.44 (m, 8H; CH_2), 1.00 ppm (t, $J(P,P) = 7.2$ Hz, 12H; CH_3); elemental analysis calcd (%) for $C_{64}H_{42}Au_3F_{35}ClNP_2$: C 35.29, H 1.94, N 0.64; found: C 35.01, H 1.87, N 0.63. $\Lambda_M = 100\ \Omega^{-1}cm^2mol^{-1}$.

Synthesis of [$\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH_2)\{\mu\text{-}Au(C_6F_5)_2\}$] (4): [$Au(C_6F_5)_2(acac)$][42] (0.2 mmol, 0.126 g) was added to a freshly prepared solution of **1** (0.2 mmol, 0.168 g) in dichloromethane (20 mL). After 1 h of stirring, the solvent was partially evaporated and hexane was added to afford **4** as a yellow solid. Yield: 65 %; ^{31}P NMR ($CDCl_3$): $\delta = -8.4$ (d, $J(P,H) = 434$ Hz, 1P; $PHAuR_3$), −32.6 ppm (t, $J(P,H) = 398$ Hz, 1P; PH_2); ^{19}F NMR ($CDCl_3$): $\delta = -119.1$ (m, 2F; o-F), −156.6 (t, $^3J(F_p,F_m) =$

19.6 Hz, 1F; *p*-F), −162.9 (m, 2F; *m*-F), −120.0 (m, 4F; *o*-F), −155.2 (t, $^3J(F_p,F_m)=19.5$ Hz, 2F; F_p), −159.8 (m, 4F; *m*-F), −121.8 (m, 2F; *o*-F), −152.6 (t, $^3J(F_p,F_m)=19.9$ Hz, 1F; *p*-F), −158.6 (m, 2F; *m*-F), −121.8 (m, 2F; *o*-F), −153.1 (t, 1F; $^3J(F_p,F_m)=19.9$ Hz, *p*-F), −161.2 ppm (m, 2F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=8.18$–7.15 (m, 4H; Ph), 6.46 (d, $J(P,H)=442$ Hz, 2H; P*H*AuR$_3$), 6.07 ppm (d, $J(P,H)=400$ Hz, 1H; PH_2); elemental analysis calcd (%) for $C_{36}H_7Au_2F_{25}P_2$: C 31.55, H 0.51; found: C 32.16, H 0.75; $\Lambda_M=60\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Synthesis of PPN[{Au(C_6F_5)$_3$}(1,2-PHC_6H_4PH){Au(C_6F_5)$_3$}{μ-Au(C_6F_5)$_2$}] (5): [Au(acac)(C_6F_5)$_2$][42] (0.2 mmol, 0.126 g) was added to a freshly prepared solution of **2** (0.2 mmol, 0.415 g) in dichloromethane (20 mL). After stirring for 1 h, partial evaporation of the solvent and addition of hexane led to the precipitation of **5** as a pale yellow solid. Yield: 71%; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=21.1$ (s, 2P, PPN), −21.0 ppm (s, 2P, *P*HAuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-119.7$ (m, 2F; *o*-F), −157.9 (t, $^3J(F_p,F_m)=19.6$ Hz, 1F; *p*-F), −162.9 (m, 2F; *m*-F), −121.1 (m, 4F; *o*-F), −158.7 (t, $^3J(F_p,F_m)=19.9$ Hz, 2F; *p*-F), −163.2 (m, 4F; *m*-F), −122.0 (m, 2F; *o*-F), −157.9 (t, $^3J(F_p,F_m)=19.7$ Hz, 1F; *p*-F), −163.8 (m, 2F; *m*-F), −122.5 (m, 4F; *o*-F), −158.7 (t, $^3J(F_p,F_m)=20.0$ Hz, 2F; *p*-F), −164.0 (m, 4F; *m*-F) −121.1 (m, 4F; *o*-F), −158.7 (t, $^3J(F_p,F_m)=19.9$ Hz, 2F; *p*-F), −163.6 ppm (m, 4F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=7.93$–7.32 (m, 34H; Ph), 6.11 (d, $J=363$ Hz, 2H; P*H*AuR$_3$); elemental analysis calcd (%) for $C_{90}H_{36}Au_3F_{40}NP_4$: C 41.48, H 1.39, N 0.54; found: C 42.18, H 1.85, N 0.59; $\Lambda_M=94\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Synthesis of PPN[{Au(C_6F_5)$_3$}(1,2-PHC_6H_4PH){Au(C_6F_5)$_3$}{μ-Au(PPh$_3$)}] (6): [Au(acac)(PPh$_3$)][43] (0.2 mmol, 0.112 g) was added to a solution of compound **2** (0.2 mmol, 0.415 g) in dichloromethane (20 mL). After 1 h of stirring the solvent was evaporated and the addition of hexane led to the isolation of **6** as a pale yellow solid. Yield: 56%. ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=45.5$ (t, $J(P,P)=145$ Hz, 1P; Au*P*Ph$_3$), 21.1 (s, 2P; PPN), −11.9 ppm (d, $J(P,P)=145$ Hz, 2P; *P*HAuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-119.7$ (m, 4F; *o*-F), −160.2 (t, $^3J(F_p,F_m)=19.8$ Hz, 2F; *p*-F), −162.8 (m, 4F; *m*-F), −120.6 (m, 4F; *o*-F), −160.2 (t, $^3J(F_p,F_m)=19.8$ Hz, 2F; *p*-F), −162.8 (m, 4F; *m*-F), −121.1 (m, 4F; *o*-F), −160.3 (t, $^3J(F_p,F_m)=20.1$ Hz, 2F; *p*-F), −162.3 ppm (m, 4F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=7.85$–7.00 (m, 49H; Ph), 5.52 (m, 2H; P*H*AuR$_3$); elemental analysis calcd (%) for $C_{96}H_{51}Au_3F_{30}NP_5$: C 45.50, H 2.03, N 0.55; found: C 44.85, H 2.32, N 0.64; $\Lambda_M=77\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Synthesis of PPN[{Au(C_6F_5)$_3$}(1,2-PHC_6H_4PH){Au(C_6F_5)$_3$}{μ-Au(PMe$_3$)}] (7): A solution of **2** (0.2 mmol, 0.415 g) in dichloromethane (10 mL) was added to a solution of [AuCl(PMe$_3$)][44] (0.2 mmol, 0.061 g) and Tl(acac)[43] (0.2 mmol, 0.061 g) in dichloromethane (10 mL). After 1 h of stirring, the mixture was filtered over Celite to remove the insoluble TlCl. Concentration of the resulting solution and addition of hexane (20 mL) led to the precipitation of **7** as a yellow solid. Yield: 71%; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=21.1$ (s, 2P, PPN), −3.6 (dd, $J(P,P)=145$ Hz, 1P; Au*P*Me$_3$), −12.1 ppm (m, 2P; *P*HAuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-119.4$ (m, 4F, *o*-F), −160.4 (t, $^3J(F_p,F_m)=19.1$ Hz, 2F; *p*-F), −162.5 (m, 4F; *m*-F), −120.6 (m, 4F; *o*-F), −160.3 (t, $^3J(F_p,F_m)=19.9$ Hz, 2F; F_p), −162.5 (m, 4F; *m*-F), −120.6 (m, 4F; *o*-F), −160.3 (t, $^3J(F_p,F_m)=19.9$ Hz, 2F; *p*-F), −162.5 ppm (m, 4F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=7.70$–6.90 (m, 34H; Ph), 5.48 (m, 2H; P*H*AuR$_3$), 1.63 ppm (s, 9H; CH_3); elemental analysis calcd (%) for $C_{81}H_{45}Au_3F_{30}NP_5$: C 41.43, H 1.93, N 0.60; found: C 40.50, H 1.60, N 0.96; $\Lambda_M=81\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Synthesis of PPN[{Au(C_6F_5)$_3$}(1,2-PHC_6H_4PH){Au(C_6F_5)$_3$}{μ-Ag(PPh$_3$)}] (8): [Ag(TfO)(PPh$_3$)] (TfO = trifluoromethylsulfonate) (0.2 mmol, 0.104 g) and PPN(acac)[41] (0.2 mmol, 0.127 g) were added to a freshly prepared solution of **2** (0.2 mmol, 0.415 g) in dichloromethane (20 mL). After stirring for 1 h, evaporation of the solvent to about 5 mL and addition of diethyl ether (20 mL) led to the precipitation of PPNTfO as a white solid, which was filtered off. Further addition of hexane led to the precipitation of **8** as a white solid. Yield: 35%; ^{31}P{^{1}H} NMR ($CDCl_3$, 223 K): $\delta=21.1$ (s, 2P; PPN), 10.5 (m, 1P; Ag*P*Ph$_3$), −69.3 ppm (m, 2P; *P*HAuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-118.5$ (m, 4F; *o*-F), −160.5 (t, $^3J(F_p,F_m)=20.2$ Hz, 2F; *p*-F), −162.5 (m, 4F; *m*-F), −119.8 (m, 4F; *o*-F), −160.5 (t, $^3J(F_p,F_m)=20.2$ Hz, 2F; F_p), −162.8 (m, 4F; *m*-F), −120.7 (m, 4F; *o*-F), −160.6 (t, $^3J(F_p,F_m)=20.3$ Hz, 2F; *p*-F), −162.9 ppm (m, 4F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=7.70$–6.90 (m, 49H; Ph), 4.29 ppm (m, 2H; P*H*AuR$_3$); elemental analysis calcd (%) for $C_{96}H_{51}Au_2AgF_{30}NP_5$: C 47.16, H 2.10, N 0.57; found: C 50.73, H 2.53, N 0.83; $\Lambda_M=86\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Synthesis of (PPN)$_2$[{Au(C_6F_5)$_3$}(1,2-PHC_6H_4PH){Au(C_6F_5)$_3$}{μ-Au(C_6F_5)}] (9): [Au(C_6F_5)(tht)][45] (0.2 mmol, 0.090 g) and PPN(acac)[41] (0.2 mmol, 0.127 g) were added to a freshly prepared solution of **2** (0.2 mmol, 0.415 g) in dichloromethane (20 mL). After 1 h of stirring, the solvent was partially evaporated and hexane was added to afford **9** as a pale yellow solid. Yield: 48%; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=21.1$ (s, 4P; PPN), −34.7 (s, 2P; *P*HAuR$_3$, one pair of isomers), −38.3 (s, 2P, *P*HAuR$_3$, the other pair of isomers); ^{19}F NMR ($CDCl_3$): $\delta=-115.3$ (m, 2F; *o*-F), −161.4 (t, 1F; $^3J(F_p,F_m)=20.5$ Hz, *p*-F), −162.6 (m, 2F; *m*-F), −117.9 (m, 2F; *o*-F), −160.4 (t, $^3J(F_p,F_m)=20.4$ Hz, 1F; F_p), −162.9 (m, 2F; *m*-F), −119.6 (m, 2F; *o*-F), −160.4 (t, $^3J(F_p,F_m)=19.3$ Hz, 1F; *p*-F), −162.9 (m, 2F; *m*-F), −119.8 (m, 4F; *o*-F), −160.5 (t, $^3J(F_p,F_m)=19.5$ Hz, 2F; *p*-F), −163.7 (m, 4F; *m*-F), −120.3 (m, 2F; *o*-F), −160.5 (t, $^3J(F_p,F_m)=19.5$ Hz, 1F; *p*-F), −162.9 (m, 2F; *m*-F), −120.4 (m, 2F; *o*-F), −160.9 (t, $^3J(F_p,F_m)=20.1$ Hz, 1F; *p*-F), −163.7 (m, 2F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=7.99$–7.20 ppm (m, 64H; Ph); elemental analysis calcd (%) for $C_{120}H_{66}Au_3F_{35}N_2P_6$: C 48.41, H 2.23, N 0.94; found: C 47.57, H 1.99, N 0.89; $\Lambda_M=155\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Synthesis of (PPN)$_2$[{Au(C_6F_5)$_3$}$_2$(1,2-PHC_6H_4PH){Au(C_6F_5)$_3$}] (10): [Au(C_6F_5)$_3$(tht)] (0.2 mmol, 0.157 g) and PPN(acac)[41] (0.2 mmol, 0.127 g) were added to a freshly prepared solution of **2** (0.2 mmol, 0.415 g) in dichloromethane (20 mL). After 1 h stirring, the solvent was partially evaporated and hexane was added to afford **10** as a yellow solid. Yield: 55%; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=21.1$ (s, 4P; PPN), −58.0 (m, 1P; *P*H(AuR$_3$)$_2$), −63.2 (m, 1P; *P*HAuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-120.1$ (m, 12F; *o*-F), −156.5 (t, $^3J(F_p,F_m)=19.8$ Hz, 2F; *p*-F), −157.0 (t, $^3J(F_p,F_m)=18.9$ Hz, 2F; *p*-F), −158.1 (t, $^3J(F_p,F_m)=19.5$ Hz, 2F; *p*-F), −162.3 (m, 4F; *m*-F), −162.8 (m, 8F; *m*-F), −120.7 (m, 2F; *o*-F), −158.8 (t, $^3J(F_p,F_m)=18.8$ Hz, 1F; F_p), −162.3 (m, 2F; *m*-F), −121.5 (m, 2F; *o*-F), −159.8 (t, $^3J(F_p,F_m)=20.1$ Hz, 1F; *p*-F), −162.3 (m, 2F; *m*-F), −121.8 (m, 2F; *o*-F), −160.7 (t, $^3J(F_p,F_m)=20.0$ Hz, 1F; *p*-F), −162.3 (m, 2F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=7.65$–7.34 ppm (m, 64H; Ph); elemental analysis calcd (%) for $C_{132}H_{66}Au_3F_{45}N_2P_6$: C 47.87, H 2.01, N 0.85; found: C 47.49, H 2.18, N 0.89; $\Lambda_M=174\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Synthesis of [{Au(C_6F_5)$_3$}{Au(PPh$_3$)}(1,2-PHC_6H_4PH){Au(C_6F_5)$_3$}{Au(PPh$_3$)}] (11): [(μ-Cl){Au(PPh$_3$)}$_2$)]ClO$_4$[46] (0.2 mmol, 0.165 g) was added to a solution of compound **2** (0.2 mmol, 0.415 g) in dichloromethane (20 mL). After 1 h of stirring, the solvent was evaporated and addition of diethyl ether (25 mL) led to the precipitation of PPN(ClO$_4$). The mixture was filtered off to separate this compound. Later, addition of hexane afforded **11** as a yellow solid. Yield: 48%; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=44.7$ (d, $^2J(P,P)=303$ Hz, 2P; Au*P*Ph$_3$), −37.1 ppm (d, $J(P,P)=303$ Hz, 2P; *P*HAuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-119.0$ (m, 4F; *o*-F), −120.1 (m, 4F; *o*-F), −158.0 (t, $^3J(F_p,F_m)=19.0$ Hz, 4F; *p*-F), ∼−161.2 (m, 8F; *m*-F), ∼−121.1 (m, 4F; *o*-F), −158.6 (t, $^3J(F_p,F_m)=19.6$ Hz, 2F; *p*-F), ∼−161.9 ppm (m, 4F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=7.68$–7.32 (m, 34H; Ph), ∼6.3 ppm (d, $J(P,H)=364$ Hz, 2H; P*H*AuR$_3$); elemental analysis calcd (%) for $C_{78}H_{36}Au_4F_{30}P_4$: C 38.16, H 1.48; found: C 38.90, H 1.42; $\Lambda_M=48\ \Omega^{-1}\,cm^2\,mol^{-1}$.

Synthesis of [{Au(C_6F_5)$_3$}(1,2-PC_6H_4P){Au(C_6F_5)$_3$}{μ-Au(dppe)Au}$_2$] (12): A solution of [(AuCl)$_2$(dppe)][47] (0.4 mmol, 0.345 g), PPN(acac)[41] (0.6 mmol, 0.382 g) and AgClO$_4$ (0.8 mmol, 0.166 g) in diethyl ether (10 mL) was added to a solution of **2** (0.2 mmol, 0.415 g) in dichloromethane (20 mL). After 1 h of stirring, the solvent was eliminated by evaporation and diethyl ether (25 mL) was added. In this way, a PPN(ClO$_4$) and AgCl mixture was precipitated. The resulting solution obtained by filtration contained the compound **12**, which was isolated by addition of hexane (yellow solid). Yield: 58%; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta=35$ (m, 4P; dppe), −13.6 ppm (m, 2P; *P*AuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-118.9$ (m, 4F; *o*-F), −157.7 (t, $^3J(F_p,F_m)=20.7$ Hz, 2F; *p*-F), −161.3 (m, 2F; *m*-F), −161.7 (m, 2F; *m*-F), −122.0 (m, 8F; *o*-F), −158.2 (t, $^3J(F_p,F_m)=19.4$ Hz, 1F; *p*-F), −159.0 (t, $^3J(F_p,F_m)=19.4$ Hz, 1F; *p*-F), −159.3 (t, $^3J(F_p,F_m)=20.8$ Hz, 1F; *p*-F), −159.5 (t, $^3J(F_p,F_m)=20.5$ Hz, 1F; *p*-F), −161.7 (m, 4F; *m*-F), −162.2 (m, 2F; *m*-F), −162.4 ppm (m, 2F; *m*-F); ^{1}H NMR ($CDCl_3$): $\delta=8.25$–6.35 (m, 44H; Ph), ∼2.7 ppm (m, 8H; CH_2); elemental

Table 4. Details of data collection and structure refinement for complexes **3**, **12** and **13**.

	3	**12**	**13**
formula	$C_{64}H_{42}Au_3ClF_{35}NP_2{\cdot}0.25\,CHCl_3$	$C_{94}H_{52}Au_6F_{30}P_6{\cdot}OC_4H_8$	$C_{94}H_{52}Ag_4Au_6F_{30}P_6{\cdot}0.5\,CHCl_3$
crystal habit	colourless cube	yellow irregular prismatic block	yellow prism
crystal size [mm]	0.15 × 0.15 × 0.15	0.3 × 0.25 × 0.22	0.35 × 0.2 × 0.17
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	13.8113(2)	27.7132(4)	27.6922(5)
b [Å]	16.4576(2)	13.2258(2)	13.0705(3)
c [Å]	17.5704(3)	33.0625(7)	32.7184(6)
α [°]	80.305(1)	90	90
β[°]	84.338(1)	125.166(1)	124.333(1)
γ [°]	71.936(1)	90	90
V [Å^3]	3738.09(10)	9906.6(3)	9779.2(3)
Z	2	4	4
ρ_{calcd} [g cm^{-3}]	1.962	2.140	1.913
M_r	2208.12	3191.08	2816.73
$F(000)$	2093	5960	5382
T [°C]	−100	−100	−100
$2\theta_{max}$/°	57	56	56
$\mu(Mo_{K\alpha})$ [mm^{-1}]	6.104	9.053	4.016
reflns measured	17741	59025	44777
unique reflns	15730	17768	11622
R_{int}	0.0581	0.0540	0.0351
R [$F>2\sigma(F)$][a]	0.0433	0.0409	0.0673
wR (F^2, all data)[b]	0.1027	0.0897	0.1797
reflns used	15730	17768	11071
parameters	975	1265	1241
restraints	389	282	484
S[c]	1.023	1.079	1.078
max residual electron density [e Å^{-3}]	1.656	1.329	4.632

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

analysis calcd (%) for $C_{94}H_{52}Au_6F_{30}P_6$: C 36.20, H 1.68; found: C 35.84, H 1.74; $\Lambda_M=40\ \Omega^{-1}cm^2mol^{-1}$.

Synthesis of [{Au(C_6F_5)$_3$}(1,2-PC_6H_4P){Au(C_6F_5)$_3$}{μ-Ag(dppe)Ag}$_2$] (13): A solution of [Ag_2dppe](TfO)$_2$ (0.4 mmol, 0.365 g) and PPN(acac)[41] (0.6 mmol, 0.382 g) in diethyl ether (10 mL) was added to a solution of **2** (0.2 mmol, 0.415 g) in dichloromethane (20 mL). After 1 h of stirring, the solvent was eliminated by evaporation and diethyl ether (25 mL) was added. In this way PPN(ClO_4) formed was precipitated and isolated. The resulting solution obtained by filtration contained compound **13**, which was obtained as a yellow solid by addition of hexane. Yield: 72%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=\sim2$ (m, 4P; dppe), ~-80 ppm (m, 2P; *P*AuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-120.6$ (m, 4F; *o*-F), −159.8 (t, $^3J(F_p,F_m)=19.5$ Hz, 2F; *p*-F), −162.5 (m, 4F; *m*-F), −120.6 (m, 4F; *o*-F), −160.0 (t, $^3J(F_p,F_m)=20.1$ Hz, 2F; *p*-F), −162.8 (m, 4F; *m*-F), −121.8 (m, 4F; *o*-F), −160.0 (t, $^3J(F_p,F_m)=20.1$ Hz, 2F; *p*-F), −162.8 ppm (m, 4F; *m*-F); ^1H NMR ($CDCl_3$): $\delta=7.90$–6.65 (m, 44H; Ph), ~2.7 ppm (m, 8H; C*H*$_2$); elemental analysis calcd (%) for $C_{94}H_{52}Ag_4Au_2F_{30}P_6$: C 40.87, H 1.90; found: C 39.70, H 1.57; $\Lambda_M=38\ \Omega^{-1}cm^2mol^{-1}$.

Synthesis of [{Au(C_6F_5)$_3$}(1,2-PC_6H_4P){Au(C_6F_5)$_3$}{μ-Cu(dppe)Cu}$_2$] (14): A solution of [Cu_2dppe](TfO)$_2$ (0.4 mmol, 0.329 g) and PPN(acac)[41] (0.6 mmol, 0.382 g) in diethyl ether (10 mL) was added to a solution of **2** (0.2 mmol, 0.415 g) in dichloromethane(20 mL). After 1 h of stirring, the solvent was eliminated by evaporation and diethyl ether (25 mL) was added. In this way, the PPN(ClO_4) formed was precipitated and isolated by filtration. The resulting solution contained compound **14**, which was isolated by evaporation of the solvent and addition of hexane to afford a yellow solid. Yield: 72%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=6$ (m, 4P; dppe), ~−50 ppm (m, 2P; *P*AuR$_3$); ^{19}F NMR ($CDCl_3$): $\delta=-119.0$ (m, 4F; *o*-F), −160.4 (m, 2F; *p*-F), −163.1 (m, 4F; *m*-F), −119.8 (m, 8F; *o*-F), −160.7 (t, $^3J(F_p,F_m)=20.3$ Hz, 4F; *p*-F), −163.6 ppm (m, 8F; *m*-F); ^1H NMR ($CDCl_3$): $\delta=7.75$–6.70 (m, 44H; Ph), ~2.7 ppm (m, 8H; C*H*$_2$); elemental analysis calcd (%) for $C_{94}H_{52}Au_2Cu_4F_{30}P_6$: C 43.67, H 2.03; found: C 45.04, H 2.48; $\Lambda_M=22\ \Omega^{-1}cm^2mol^{-1}$.

Crystallography: The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Nonius Kappa CCD diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected using monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Scan type ω and φ. Absorption corrections: numerical (based on multiple scans). The structures were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 using the program SHELXL-97.[48] All non-hydrogen atoms were refined anisotropically except the molecules of solvent. Hydrogen atoms were included by using a riding model. Selected bond lengths and angles are collected in Tables 1–3 and the crystal structures of **3**, **12** and **13** are shown in Figures 1–3, respectively. Further details of the data collection and refinement are given in Table 4. CCDC–28823–288232 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Special details: In compound **12** the solvent molecule (tetrahydrofuran) was disordered. A reasonable disorder model involved two different positions (0.65:0.35).

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