Heteropolynuclear Phosphide Complexes: Phosphorus as Unique Atom Bridging Coinage Metal Centres

M. Carmen Blanco,[b] Eduardo J. Fernández,[b] José M. López-de-Luzuriaga,[b] M. Elena Olmos,[b] Olga Crespo,[a] M. Concepción Gimeno,[a] Antonio Laguna,*[a] and Peter G. Jones[c]

Dedicated to Professor Hubert Schmidbaur on the occasion of his 65th birthday

Abstract: In this paper we describe the synthesis and reactivity of the diphenylphosphine derivatives $[Au(C_6F_5)(PPh_2H)]$ and *trans*-$[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$. Reactions of the latter or the neutral $[Au(C_6F_5)_3(PPh_2H)]$ with the appropriate Group 11 metal reagents (M = Au, Ag, Cu) in the presence of acetylacetonate afford a series of novel Au^{III}-M phosphido-bridged complexes, which have been scarcely represented to date. The crystal structure of the tetranuclear $[\{Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Ag\}_2]$ and the dinuclear $[Au(C_6F_5)_3(\mu\text{-}PPh_2)M(PPh_3)]$ (M = Au, Ag) complexes were established by X-ray diffraction methods. The synthesis and deprotonating activity of the anionic gold(III) complex $PPN[Au(C_6F_5)_3(acac)]$ (PNN = $[N(PPh_3)_2]^+$) was studied.

Keywords: copper · gold · phosphides · polycycles · silver

Introduction

One of the most important features in the chemistry of gold[1] is the tendency of the metal to display short contacts or interactions in the solid state.[2] These have been attributed to correlation effects that are strengthened by relativistic effects, which are in turn most marked in the case of gold(I).[3] Apart from its fundamental interest, this aurophilic attraction[4] may play a role in the medical applications of gold compounds[5] or be associated with useful optical properties.[6]

The most common strategy for the synthesis of polynuclear complexes that can display gold–gold interactions is the use of polydentate ligands.[3g, 7] The formation of monoatomic bridges has also been useful to obtain polynuclear gold(I) derivatives;[8] in the case of gold(III), although some doubly bridged $[Au_2R_4(\mu\text{-}X)_2]$ (R = alkyl, aryl; X = Cl, Br, I, N_3, NCO, NMe_2, NHMe, SEt) species are known,[9] only recently have the first examples of $[(AuR_3)_2(\mu\text{-}X)]$ (X = monoatomic bridging ligand) been reported.[10]

The chemistry of phosphido-bridged transition metals of Groups 8–10 has experienced considerable development in the last few years,[11–13] whereas few corresponding investigations of Group 11 metals have been reported since $[\{AuPPh_2\}_n]$ was first prepared in 1976.[14] Particularly in the case of gold, very few metal(I) derivatives that contain PR_2H[15] or PR_2^- ligands[14–16] are known. The chemistry of gold(III) is even less well represented: only the dinuclear complex $[Au_2Me_4(\mu\text{-}PPh_2)_2]$[14] had been reported until we started our research in this field.

We have recently reported the synthesis of the first gold(III) complex that contains a secondary phosphine, and its utility as a precursor for the preparation of unprecedented Au^{III}-M phosphides.[17] In the course of our investigations, we have now succeeded in the synthesis of the diphenylphosphine gold derivatives $[Au(C_6F_5)(PPh_2H)]$ and *trans*-$[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$. The latter gold(III) species has also proved to be a good precursor for the preparation of novel Au^{III}-M phosphides, such as the set of tetranuclear complexes $[\{Au(C_6F_5)_2(\mu\text{-}PPh_2)_2M\}_2]$ (M = Cu, Ag, Au), the trinuclear $PPN[\{Au(C_6F_5)_2(\mu\text{-}PPh_2)_2\}_2Cu]$ (PPN = $[N(PPh_3)_2]^+$), *trans*-

[a] Prof. Dr. A. Laguna, Dr. O. Crespo, Dr. M. C. Gimeno
Departamento de Química Inorgánica
Instituto de Ciencia de Materiales de Aragón
Universidad de Zaragoza-CSIC, 50009 Zaragoza (Spain)
Fax: (+34) 976-761187
E-mail: alaguna@posta.unizar.es

[b] M. C. Blanco, Dr. E. J. Fernández, Dr. J. M. López-de-Luzuriaga, Dr. M. E. Olmos
Departamento de Química, Universidad de La Rioja
Grupo de Síntesis Química de La Rioja, UA-CSIC
Madre de Dios 51, 26004 Logroño (Spain)

[c] Prof. Dr. P. G. Jones
Institüt für Anorganische und Analytische Chemie
der Technischen Universität
Postfach 3329, 38023 Braunschweig (Germany)

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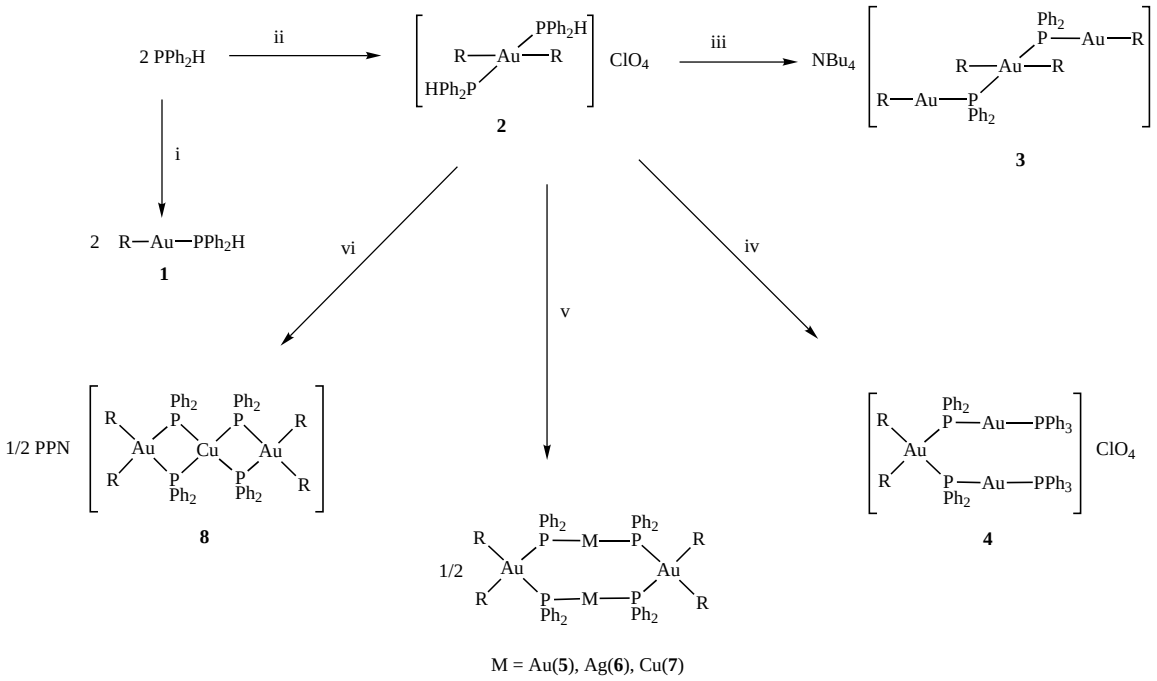

Scheme 1. $R = C_6F_5$; i) 2 [AuR(tht)]; ii) $[AuR_2(OEt_2)_2]ClO_4$; iii) 2 [AuR(tht)] + 2 NBu_4(acac); iv) 2 [Au(acac)(PPh_3)] or ⅔ $[O(AuPPh_3)_3]ClO_4$; v) PPN[Au(acac)$_2$], $AgClO_4$ + 2 PPN(acac) or $[Cu(NCMe)_4]TfO$ + 2 PPN(acac); vi) ½ $[Cu(NCMe)_4]TfO$ + 2 PPN(acac).

$NBu_4[Au(C_6F_5)_2\{(\mu\text{-}PPh_2)Au(C_6F_5)\}_2]$ or *cis*-$[Au(C_6F_5)_2\{(\mu\text{-}PPh_2)Au(PPh_3)\}_2]ClO_4$, or the dinuclear $[Au(C_6F_5)_3(\mu\text{-}PPh_2)M(PPh_3)]$ (M = Au, Ag).

Furthermore, we have been able to prepare the C-bonded acetylacetonate gold(III) complex PPN[$Au(C_6F_5)_3$(acac)] in order to study its ability as a deprotonating agent in the synthesis of gold(III) phosphides. To the best of our knowledge, this is the first reported triarylalkylaurate(III) derivative.[9]

Results and Discussion

The diphenylphosphanylgold(I) complex $[Au(C_6F_5)(PPh_2H)]$ (**1**) was obtained by the displacement of the weakly coordinated tetrahydrothiophene (tht) ligand from $[Au(C_6F_5)(tht)]$ when treated with the free phosphine in equimolecular amounts (Scheme 1). Complex **1** is isolated as a moderately air- and moisture-stable white solid that is soluble in chlorinated solvents, diethyl ether and acetone, and is insoluble in hexane. It is nonconducting in acetone solutions. Its IR spectrum shows absorptions arising from the $C_6F_5^-$ anion bonded to a gold(I) centre.[18] In its mass spectrum ($LSIMS^+$), although the molecular peak does not appear, a peak corresponding to the fragment $[Au(PPh_2H)]^+$ is observed at *m*/*z* 383 (50 %).

The $^{31}P\{^1H\}$ NMR spectrum of **1** displays a singlet at $\delta = 11.8$ that is shifted to low field relative to the signal of the free ligand at $\delta = -40.3$, and the ^{19}F NMR spectrum shows the three typical resonances of pentafluorophenyl groups bonded to gold(I). Furthermore, the ^1H NMR spectrum displays one signal of the expected doublet at $\delta = 6.31$, while the second is probably located in the same region as the aromatic protons.

When the free PPh_2H ligand is added to a solution of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ in a 2:1 molar ratio, the novel derivative *trans*-$[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$ (**2**) is obtained, which is the second diphenylphosphanylgold(III) complex described to date. Complex **2** is an air- and moisture-stable white solid at room temperature and is soluble in chlorinated solvents and acetone, and insoluble in diethyl ether and hexane. It behaves as a univalent electrolyte in acetone solutions.

In its IR spectrum, in addition to the characteristic bands of the perchlorate anion,[19] there are three vibrations corresponding to pentafluorophenyl groups bonded to gold(III) at $\tilde{\nu} = 1511$ (vs), 967 (vs) and 800 cm^{-1} (s). This last signal appears as unique narrow band, which is in accordance with a *trans* disposition of the ligands.[18]

Abstract in Spanish: *En el presente trabajo se describe la síntesis y estudio de la reactividad de los difenilfosfino derivados $[Au(C_6F_5)(PPh_2H)]$ y trans-$[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$. El tratamiento de este último o del derivado neutro $[Au(C_6F_5)_3(PPh_2H)]$ con los sustratos adecuados de metales del grupo 11 en presencia del anión acetilacetonato conduce a la obtención de complejos mixtos Au^{III}-M con ligandos fosfuro puente, que hasta la fecha se encuentran muy poco representados. Se han determinado por difracción de rayos X las estructuras cristalinas de los derivados dinucleares $[Au(C_6F_5)_3(\mu\text{-}PPh_2)M(PPh_3)]$ (M = Au, Ag) y la del compuesto tetranuclear $[Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Ag]_2$. Por último, se describe la síntesis del derivado aniónico de oro(III) PPN$[Au(C_6F_5)_3(acac)]$, cuya actividad como agente desprotonante ha sido también estudiada.*

This arrangement is also confirmed in its $^{31}P\{^1H\}$ NMR spectrum: the singlet at $\delta = -8.6$ is not broadened as in **1**, in which the phosphorus is located in a *trans* position to a C_6F_5 group. Its ^{19}F NMR spectrum shows three resonances from the *ortho*, *meta* and *para* fluorine atoms of pentafluorophenyl groups bonded to gold(III) and in its ^1H NMR spectrum only one signal of the expected doublet is clearly observed, while the second is probably masked by the aromatic protons.

As mentioned above, our interest is focused not only on the synthesis of new diphenylphosphine compounds, but also on their utilisation as starting materials in the preparation of phosphido-bridged gold species. Thus, the reaction of **2** with $[Au(C_6F_5)(tht)]$ and $NBu_4(acac)$ (1:2:2 molar ratio) or with two equivalents of $[Au(acac)(PPh_3)]$ leads to the formation of the trinuclear mixed Au^I-Au^{III}-Au^I phosphides, namely *trans*-$NBu_4[Au(C_6F_5)_2\{(\mu\text{-}PPh_2)Au(C_6F_5)\}_2]$ (**3**) or *cis*-$[Au(C_6F_5)_2\{(\mu\text{-}PPh_2)Au(PPh_3)\}_2]ClO_4$ (**4**) (Scheme 1). Complex **4** can also be prepared from $[O(AuPPh_3)_3]ClO_4$ (3:2 molar ratio) instead of $[Au(acac)(PPh_3)]$ as the deprotonating/aurating agent.

Complexes **3** and **4** are obtained as stable white solids, soluble in most common solvents, but insoluble in hexane; compound **4** is also insoluble in diethyl ether. Both of them behave as univalent electrolytes in acetone solutions and their analytical and spectroscopic data are in accordance with the proposed stoichiometries.

Their IR spectra, in addition to the NBu_4^+ (**3**) or ClO_4^- (**4**) absorptions at $\tilde{\nu} = 880$ (m, br) (**3**) or 1090 (vs, br) and 623 cm^{-1} (m) (**4**), show bands at $\tilde{\nu} = 1505$ (vs), 964 (vs) and 788 (s) (**3**) or 1505 (vs), 962 (vs) and 794 cm^{-1} (m, br) (**4**) assignable to the pentafluorophenyl groups bonded to gold(III).[18] The last of the three bands seems to indicate a *trans* arrangement of the ligands in the case of complex **3**, while its appearance as a broad absorption in complex **4** suggests a *cis* arrangement; this implies a *trans*/*cis* isomerisation. A strong band at $\tilde{\nu} =$ 954 cm^{-1}, which corresponds to C_6F_5 groups bonded to gold(I), appears in the IR spectrum of **3**.

The $^{31}P\{^1H\}$ NMR of complex **3** shows a singlet at $\delta = 38.2$, while there is an AB system in the case of **4**, in which the signals corresponding to the phosphorus of the PPh_2 groups are broadened because of their coupling with the fluorine nuclei of C_6F_5. Their ^1H NMR spectra confirm the deprotonation of the secondary phosphine and the mass spectra (LSIMS) of both complexes show the molecular ion at *m*/*z* 1629 (5%, **3**) and 1819 (25%, **4**).

In order to increase the nuclearity of the products, we treated complex **2** with other starting materials that contain Group 11 metals, such as $PPN[Au(acac)_2]$ (1:1 molar ratio) or PPN(acac) and $AgClO_4$ or $[Cu(NCMe)_4]TfO$ ($TfO = CF_3SO_3$) (1:2:1 molar ratio) (Scheme 1). These reactions afford the new tetranuclear Au^{III}-M^I complexes $[\{Au(C_6F_5)_2(\mu\text{-}PPh_2)_2M\}_2]$ {M = Au (**5**), Ag (**6**), Cu (**7**)} that have a central eight-membered ring formed by four diphenylphosphide units and four metallic atoms. Compounds **5**–**7** are isolated as pale yellow solids that are air and moisture stable and soluble in most common organic solvents, but insoluble in hexane. They are nonconducting in acetone and their analytical and spectroscopic data agree with the proposed stoichiometry.

Their IR spectra show absorptions arising from the C_6F_5 groups bonded to gold(III) at $\tilde{\nu} = 1505$ (vs), 961 (vs) and 790 cm^{-1} (m, br). This last band is split into two, which suggests a *cis* arrangement of the C_6F_5 groups and therefore a *trans*/*cis* isomerisation, which is necessary for the formation of the ring.

Their $^{31}P\{^1H\}$ NMR spectra again display broadened signals (because of the coupling with the fluorine atoms), shifted to low field relative to the starting complex **2**, as singlets at $\delta =$ 35.5 and −2.7 for complexes **5** and **7**, respectively. In complex **6** the signal is split into two complicated multiplets because of coupling of the phosphorus with the magnetically active ^{107}Ag and ^{109}Ag isotopes of two silver centres. In their ^{19}F NMR spectra we observe again the typical pattern of a unique type of C_6F_5 group bonded to gold(III) and their ^1H NMR spectra only show resonances attributed to aromatic protons. None of the molecular peaks are detected in the mass spectra; however, several peaks corresponding to various fragments are observed (see the Experimental Section).

Layering a chloroform solution of complex **6** with hexane afforded crystals of the silver derivative which were suitable for X-ray diffraction studies. The molecule of complex **6** is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The complex crystallises with one molecule of chloroform and half a molecule of hexane. It consists of an

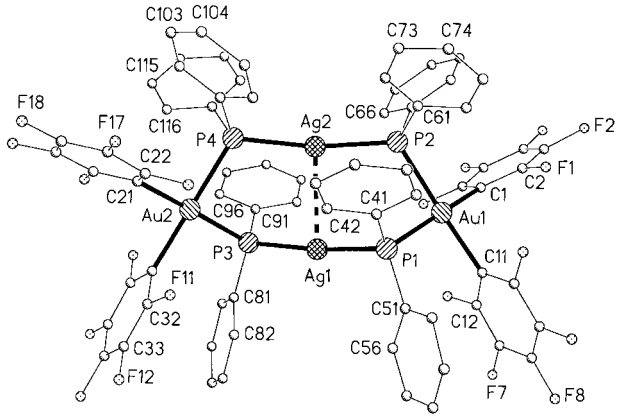

Figure 1. Molecular structure of complex **6** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

Table 1. Selected bond lengths [Å] and angles [°] for complex **6**.

Au1–C11	2.073(9)	Au1–C1	2.078(9)
Au1–P1	2.368(2)	Au1–P2	2.394(2)
Au2–C31	2.069(9)	Au2–C21	2.091(8)
Au2–P3	2.375(2)	Au2–P4	2.390(2)
Ag1–P3	2.383(2)	Ag1–P1	2.386(2)
Ag1–Ag2	2.9435(10)	Ag2–P2	2.400(2)
Ag2–P4	2.400(2)		
C11-Au1-C1	89.2(3)	C11-Au1-P1	90.5(3)
C1-Au1-P1	170.9(3)	C11-Au1-P2	177.3(3)
C1-Au1-P2	91.4(2)	P1-Au1-P2	89.29(8)
C31-Au2-C21	87.2(3)	C31-Au2-P3	91.6(2)
C21-Au2-P3	175.1(3)	C31-Au2-P4	177.7(3)
C21-Au2-P4	93.9(2)	P3-Au2-P4	87.50(8)
P3-Ag1-P1	173.02(9)	P3-Ag1-Ag2	84.05(6)
P1-Ag1-Ag2	90.65(6)	P2-Ag2-P4	169.14(9)
P2-Ag2-Ag1	92.13(6)	P4-Ag2-Ag1	96.59(6)
Au1-P1-Ag1	105.03(9)	Au1-P2-Ag2	119.12(10)
Au2-P3-Ag1	108.47(9)	Au2-P4-Ag2	115.92(10)

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eight-membered metallacycle with an alternating metal–ligand arrangement and a twisted chair conformation. There is a Ag–Ag contact of 2.9435(10) Å, which is presumably weakly bonding, whereas the Ag–Au distances of 3.773–4.133 Å are too long to be considered significant interactions. The Ag atoms are in a distorted linear environment (P4-Ag2-P2 169.14(9) and P3-Ag1-P1 173.02(9)°) that is probably associated with the Ag–Ag contact. The gold(III) centres have a very regular square-planar geometry with mean deviations for the best plane of only 0.06 Å and 0.03 Å for Au1 and Au2, respectively. The Ag–P bond lengths are 2.383(2), 2.386(2) and 2.400(2) Å and compare well with those obtained in the complex PPN[{Au(C_6F_5)$_3$(μ-PPh$_2$)}$_2$Ag] (2.386(1) Å),[17] which also contains a Ag–phosphide bond. The Au–P bond lengths lie in the range 2.368(2)–2.394(2) Å; the shorter ones are similar to those in the complexes PPN[{Au(C_6F_5)$_3$-(μ-PPh$_2$)}$_2$M] (M = Au, Ag) (2.365(2) Å) and the longer to those in PPN[{Au(C_6F_5)$_3$}$_2$(μ-PPh$_2$)] (2.390(2)–2.396(2) Å).[10b] The Au–C bond lengths of 2.069(9)–2.091(8) Å are similar to those found in other tris(pentafluorophenyl) complexes. The phosphorus atoms of the phosphide ligands have a very regular tetrahedral geometry, as expected in the absence of short Au–Ag interactions.

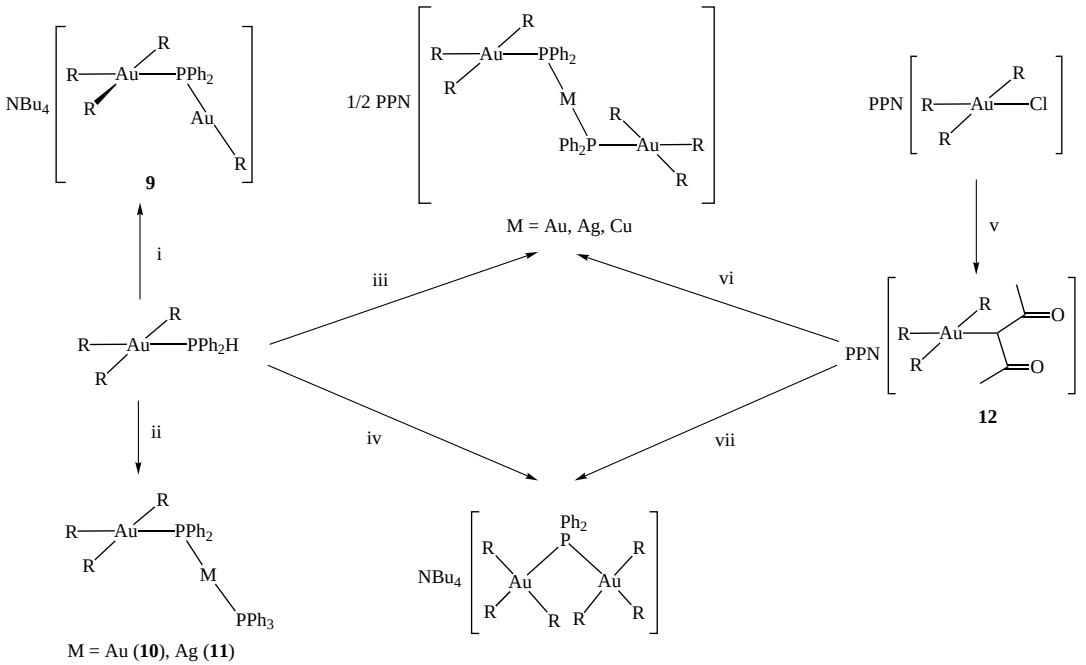
When the reaction between **2** and [Cu(NCMe)$_4$]TfO in the presence of PPN(acac) is carried out in a 2:1:4 molar ratio instead of 1:1:2, the anionic trinuclear derivative PPN[{Au(C_6F_5)$_2$(μ-PPh$_2$)$_2$}$_2$Cu] (**8**) is obtained. Complex **8** is isolated as a stable yellow solid that is soluble in chlorinated solvents, acetone and diethyl ether, and insoluble in hexane. It behaves as an univalent electrolyte in acetone solutions. Its IR spectrum shows, in addition to the bands corresponding to the pentafluorophenyl groups, a new absorption at $\tilde{\nu} = 534\ cm^{-1}$ attributed to PPh$_3$ groups of the cation.

The presence of the PPN$^+$ is clearly confirmed in its $^{31}P\{^1H\}$ NMR spectrum, in which a sharp singlet appears at $\delta = 21.1$. The resonance of the four equivalent phosphorus atoms is located at $\delta = -6.9$, which again appears as a broad singlet because of the presence of C_6F_5 groups in the *trans* position. The ^{19}F and ^1H NMR spectra of **8** are similar to those of complex **7**, and show a unique type of C_6F_5 and aromatic protons, respectively.

Complexes **5**–**7** are related to those previously reported compounds PPN[{Au(C_6F_5)$_3$(μ-PPh$_2$)}$_2$M] (M = Au, Ag, Cu), which were similarly prepared from [Au(C_6F_5)$_3$(PPh$_2$H)] instead of **2** as the starting material.[17] We therefore tried to synthesize new tris(pentafluorophenyl)gold(III) phosphides starting from [Au(C_6F_5)$_3$(PPh$_2$H)]. When this compound was treated with equimolecular amounts of [Au(C_6F_5)(tht)] and NBu$_4$(acac) in dichloromethane, the dinuclear anionic complex NBu$_4$[Au(C_6F_5)$_3$(μ-PPh$_2$)Au(C_6F_5)] (**9**) was obtained as a white solid (Scheme 2). Complex **9** behaves as a univalent electrolyte in acetone.

The $^{31}P\{^1H\}$ NMR spectrum of **9** displays a broad singlet at $\delta = 30.2$; its ^{19}F NMR spectrum shows three groups of signals attributed to the *ortho*, *para* and *meta* fluorine nuclei. In its ^1H NMR spectrum, only the resonances of the NBu$_4^+$ and aromatic protons are observed. The mass spectrum (LSIMS$^-$) displays the molecular anion at *m*/*z* 1247 (25%), with an experimental isotopic distribution in agreement with the calculated distribution.

The reaction between equimolecular amounts of [Au(C_6F_5)$_3$(PPh$_2$H)] and [Au(acac)(PPh$_3$)] or [Ag(CF_3SO_3)-(PPh$_3$)] and NBu$_4$(acac) gives the dinuclear derivatives [Au(C_6F_5)$_3$(μ-PPh$_2$)M(PPh$_3$)] {M = Au (**10**), Ag (**11**)}. They are white solids that are air and moisture stable and non-conducting in acetone solutions.



Scheme 2. R = C_6F_5; i) [AuR(tht)] + NBu$_4$(acac); ii) [Au(acac)(PPh$_3$)] or [Ag(TfO)(PPh$_3$)] + NBu$_4$(acac); iii) ½PPN[Au(acac)$_2$], ½AgClO$_4$ + PPN(acac) or ½[Cu(NCMe)$_4$]TfO + PPN(acac); iv) [AuR$_3$(tht)] + NBu$_4$(acac); v) Tl(acac); vi) ½[Au(PPh$_2$H)$_2$]TfO; vii) [AuR$_3$(PPh$_2$H)]

The $^{31}P\{^1H\}$ NMR spectrum of **10** displays an AB system centred at $\delta = 37.8$, in which the signals that correspond to the phosphorus of the diphenylphosphide (those located at higher field) appear broadened once again. In the case of complex **11**, its $^{31}P\{^1H\}$ NMR spectrum at room temperature displays very broad signals; however, when the temperature is lowered to 223 K, an AB system can be recognised, with each signal split into four because of the coupling of the phosphorus with the ^{107}Ag and ^{109}Ag nuclei. Their ^{19}F NMR spectra show the pattern characteristic of tris(pentafluorophenyl) derivatives. In their ^1H NMR spectra, only resonances from aromatic protons (and from hexane in solid **11**) are observed.

Compounds **10** and **11** (Figures 2 and 3), in contrast to $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2M]$[17] are not isotypic (**10** crystallises with disordered solvent, **11** solvent-free) and thus the comparison of metal–ligand bond angles and lengths cannot be so direct. Nevertheless, these are similar in both complexes (Table 2) and compare well with the bond lengths found in analogous compounds. The silver atom in **11** and the gold centre bonded to the triphenylphosphine ligand in **10** exhibit

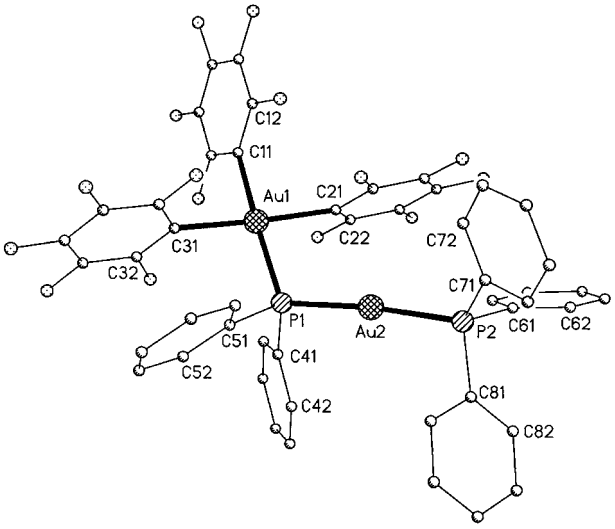


Figure 2. Molecular structure of complex **10** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

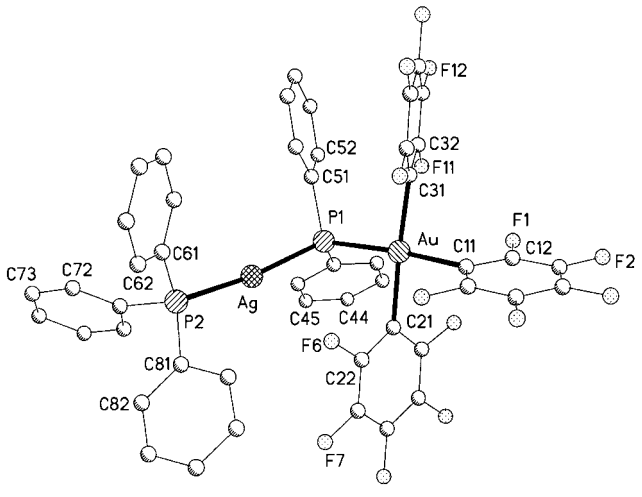


Figure 3. Molecular structure of complex **11** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

Table 2. Selected bond lengths [Å] and angles [°] for **10** and **11**.

	10 (M = Au)	**11** (M = Ag)
Au–C21	2.055(6)	2.064(3)
Au–C11	2.068(6)	2.073(3)
Au–C31	2.074(6)	2.063(3)
Au–P1	2.3734(17)	2.3821(9)
M–P2	2.3025(17)	2.4112(10)
M–P1	2.3168(16)	2.4172(10)
C21-Au-C11	88.3(2)	87.74(13)
C21-Au-C31	175.6(2)	176.27(12)
C11-Au-C31	90.6(2)	89.89(12)
C21-Au-P1	89.71(17)	88.55(10)
C11-Au-P1	177.99(17)	175.22(9)
C31-Au-P1	91.37(17)	93.96(9)
P2-M-P1	174.23(6)	170.50(3)
M-P1-Au1	116.45(6)	115.42(4)

linear geometries with P2-M-P1 angles of 174.23(6)° (**10**) and 170.50(3)° (**11**). The coordination around the other gold atom is square planar with a mean deviation of 0.05 (**10**) and 0.04 Å (**11**). In both complexes, the metal–metal distances are long, Au1–Au2 3.988 in **10** and Ag–Au 4.057 Å in **11**. The Au–C bond lengths, 2.055(6)–2.074(6) (**10**), 2.063(3)–2.073(3) Å (**11**), are similar to those found in $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2M]$[17] (M = Ag, Au: 2.052(5)–2.078(5) Å) and also to those found in other tris(pentafluorophenylgold(III) derivatives.[20–22] The Au^{III}–P bond lengths, 2.3734(17) (**10**), 2.3821(9) Å (**11**), are of the same order as those in $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2M]$ (M = Ag, Au) (2.365 Å in both complexes) or in $NBu_4[\{Au(C_6F_5)_3(Ph_2CHPPh_2)\}_2Au]$[21] (2.367(2) Å). The Au^{I}–P bond lengths in **10** (2.3025(17), 2.3168(16) Å) compare well with those found in $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2Au]$ (2.319(2) Å) or in $PPN[Mn(CO)_4\{(\mu\text{-}PPh_2)Au(C_6F_5)\}_2]$[16b] (2.313(2), 2.322(1) Å). Ag–P bond lengths in **11** (2.4112(10), 2.4171(10) Å compare well to that found in $[Ag\{P(CH_2CH_2CN)_3\}_2]NO_3$ (2.3832(9) Å), which is linear at the silver atom.[23]

Differences between the two derivatives are found in the crystal packing. The main difference is furnished by the Ag···F contacts found in **11** (3.051–3.288 Å). This type of contact between silver centres and fluorine of pentafluorophenyl rings has been widely studied and our values for **11** resemble some of the higher values described so far.[24]

The trinuclear derivatives $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2M]$ (M = Cu, Ag, Au) were obtained[17] by reaction of $[Au(C_6F_5)_3(PPh_2H)]$ with the acetylacetonate derivative $PPN[Au(acac)_2]$, which is a good deprotonating agent.[25] We have prepared the acetylacetonate derivative of gold(III), $PPN[Au(C_6F_5)_3(acac)]$ (**12**), by reaction of $PPN[Au(C_6F_5)_3Cl]$ with Tl(acac) (Scheme 2). Complex **12** is a white solid that is soluble in most common organic solvents, but insoluble in hexane. In acetone solutions it behaves as a univalent electrolyte.

Its IR spectrum shows, in addition to the absorptions corresponding to the C_6F_5 groups at $\tilde{\nu} = 1505$ (vs), 966 (vs) and 790 cm^{-1} (s, br), the ν(C=O) stretching bands of the C-bonded acetylacetonate ligand at 1673 and 1664 cm^{-1}.[26] The $^{31}P\{^1H\}$ and ^{19}F NMR spectra display the resonances arising from the PPN cation and the pentafluorophenyl groups, respectively, while in its ^1H NMR spectrum, apart from the signals

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attributed to the aromatic hydrogens, two singlets of the acetylacetonate protons appear at $\delta = 4.22$ and 2.09 with a relative integration of 1:6. The molecular anion is detected in its mass spectrum (ES^-) at m/z 797 (10%), with an experimental isotopic distribution and in accordance with that calculated.

The crystal structure of compound **12** was studied by X-ray diffraction; however, the results are rendered very imprecise by severe disorder phenomena. In view of this, we do not present full data; however, the acetylacetonate ligand is seen to be bonded to the gold centre through the C3 atom.

The reaction between $[Au(PPh_2H)_2]TfO$ and **12** (1:2) leads to the trinuclear complex $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2Au]$. Although the reaction of $[Au(C_6F_5)_3(PPh_2H)]$ with $PPN[Au(acac)_2]$ takes place at room temperature, the use of refluxing toluene and a longer time are required in this case and the yield is lower. Similarly, treatment of **12** with equimolecular amounts of $[Au(C_6F_5)_3(PPh_2H)]$ affords $PPN[\{Au(C_6F_5)_3\}_2(\mu\text{-}PPh_2)]$, which can also be obtained by reaction of $[Au(C_6F_5)_3(PPh_2H)]$, $[Au(C_6F_5)_3(tht)]$ and $NBu_4(acac)$,[10b] but under less mild conditions and in lower yield. Finally, when **12** is treated with $[Au(C_6F_5)(PPh_2H)]$ (**1**), the trinuclear species $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2Au]$ is obtained instead of complex **9**.

Experimental Section

Instrumentation: IR spectra were recorded in the range $\tilde{\nu} = 4000 - 200\ cm^{-1}$ on a Perkin–Elmer FT-IR Spectrum 1000 spectrophotometer with Nujol mulls between polyethylene sheets. Conductivities were measured in $\approx 5 \times 10^{-4}$ M acetone solutions with a Jenway 4010 conductimeter. C, H and N analysis were carried out with a Perkin–Elmer 240C microanalyser. Mass spectra were recorded on a VG Autospec by means of LSIMS techniques in a nitrobenzyl alcohol matrix, and on a HP 59987 A ELECTROSPRAY by means of ES techniques. ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX 300 in $CDCl_3$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) and H_3PO_4 (85%) ($^{31}P\{^1H\}$, external).

Solvent and reagent pretreatment: Dichloromethane and hexane were distilled from CaH_2 and diethyl ether from sodium, under nitrogen atmosphere. Diphenylphosphine and $AgClO_4$ were purchased from Aldrich. $[Cu(NCMe)_4]TfO$ was prepared as described[27] from triflic acid instead of tetrafluoroboric acid. $[Ag(TfO)(PPh_3)]$ was obtained by reaction of equimolecular amounts of $[AgCl(PPh_3)]$[28] and AgTfO.

Caution! Perchlorate salts of organic cations may be explosive.

Synthesis of $[Au(C_6F_5)(PPh_2H)]$ (1): PPh_2H (hexane solution, 0.96 M, 208 μL, 0.2 mmol) was added to a solution of $[Au(C_6F_5)(tht)]$[29] (0.090 g, 0.2 mmol) in dichloromethane (20 mL). After stirring for 1 h, the solvent was partially removed and cold hexane was added to afford **1** as a white solid (0.065 g). Yield: 59%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 11.8$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -116.4$ (m, 2F; *o*-F), -158.1 (t, $^3J(F_p,F_m) = 20.0$ Hz, 1F; *p*-F), -162.3 (m, 2F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.75 - 7.49$ (m, 10H; Ph), 6.31 (1H; $HPPh_2$); elemental analysis calcd (%) for $C_{18}H_{11}AuF_5P$: C 39.30, H 2.00; found: C 40.20, H 2.25

Synthesis of *trans*-$[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$ (2): PPh_2H (hexane solution, 0.96 M, 208 μL, 0.2 mmol) was added to a freshly prepared solution of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$[30] (0.078 g, 0.1 mmol) in diethyl ether (20 mL), and a white solid immediately appeared. The reaction mixture was stirred for 1 h and the solid filtered off (0.088 g). Yield: 88%; MS ($LSIMS^+$): m/z (%): 903 (15) $[M]^+$; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -8.6$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -120.1$ (m, 4F; *o*-F), -154.3 (t, $^3J(F_p,F_m) = 19.9$ Hz, 2F; *p*-F), -158.7 (m, 4F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 8.11$ (d, $^1J(H,P) = 463.1$ Hz, 2H), 7.49–7.32 (m, 20H; Ph); elemental analysis calcd (%) for $C_{36}H_{22}AuClF_{10}O_4P_2$: C 43.10, H 2.20; found: C 43.00, H 2.60.

Synthesis of *trans*-$NBu_4[Au(C_6F_5)_2\{(\mu\text{-}PPh_2)Au(C_6F_5)\}_2]$ (3): $[Au(C_6F_5)(tht)]$ (0.090 g, 0.2 mmol) and $NBu_4(acac)$[31] (0.068 g, 0.2 mmol) were added to a solution of compound **2** (0.1 g, 0.1 mmol) in dichloromethane (20 mL). The solution was stirred for 1 h at room temperature and concentrated to ≈5 mL. Diethyl ether (20 mL) was added to afford **3** as a white solid (0.039 g). Yield: 25%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 38.2$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -115.1$ (m, 4F; *o*-F), -160.3 (t, $^3J(F_p,F_m) = 20.2$ Hz, 2F; *p*-F), -161.7 (m, 4F; *m*-F), -120.0 (m, 4F; *o*-F), -161.6 (t, $^3J(F_p,F_m) = 20.2$ Hz, 2F; *p*-F), -163.8 (m, 4F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.57 - 7.04$ (m, 20H; Ph), 3.1 (m, 8H; CH_2), 1.6 (m, 8H; CH_2), 1.4 (m, 8H; CH_2), 1.0 (t, 12H; CH_3); elemental analysis calcd (%) for $C_{64}H_{56}Au_3F_{20}P_2N$: C 41.05, H 3.00, N 0.75; found: C 40.55, H 3.10, N 0.75.

Synthesis of *cis*-$[Au(C_6F_5)_2\{(\mu\text{-}PPh_2)Au(PPh_3)\}_2]ClO_4$ (4): This compound can be synthesised in two different ways:

Method A: $[O(AuPPh_3)_3]ClO_4$[32] (0.148 g, 0.1 mmol) was added to a solution of compound **2** (0.15 g, 0.15 mmol) in dichloromethane (20 mL), and the resulting solution was stirred at room temperature for 1 h. The solution was concentrated in vacuo, diethyl ether (20 mL) was added and a white precipitate of compound **4** was formed that was filtered off, washed with diethyl ether and dried in vacuo (0.167 g). Yield: 58%.

Method B: Compound **2** (0.1 g, 0.1 mmol) was added to a solution of $[Au(acac)(PPh_3)]$[33] (0.112 g, 0.2 mmol) in dichloromethane (20 mL). The resulting solution was stirred at room temperature for 1 h and then concentrated in vacuo to ≈5 mL. Diethyl ether was added to precipitate complex **4** as a white solid (0.088 g). Yield: 46%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 42.9$ (A, $AuPPh_3$), 37.7 (B, PPh_2) [$J(A,B) = 629.0$ Hz]; ^{19}F NMR ($CDCl_3$): $\delta = -121.7$ (m, 4F; *o*-F), -157.6 (t, $^3J(F_p,F_m) = 19.9$ Hz, 2F; *p*-F), -160.1 (m, 4F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.63 - 7.35$ (m, 50H; Ph); elemental analysis calcd (%) for $C_{72}H_{50}Au_3ClF_{10}O_4P_4$: C 45.05, H 2.60; found: C 45.75, H 2.40.

Synthesis of $[Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Au]_2$ (5): $PPN[Au(acac)_2]$[31, 33] (0.093 g, 0.1 mmol) was added to a solution of compound **2** (0.1 g, 0.1 mmol) in dichloromethane (20 mL). After 1 h of stirring the solvent was evaporated, diethyl ether was added and the mixture was filtered to remove the insoluble $PPN(ClO_4)$. The resulting yellow solution was concentrated in vacuo and cold hexane was added to afford **5** as a pale yellow solid (0.064 g). Yield: 58%; MS ($LSIMS^+$): m/z (%): 1862 (5) $[M - 2C_6F_5]^+$, 1313 (100) $[(C_6F_5)Au\{(\mu\text{-}PPh_2)Au\}_2(PPh_2)]^+$; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 35.5$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -120.7$ (m, 8F; *o*-F), -158.6 (t, $^3J(F_p,F_m) = 20.0$ Hz, 4F; *p*-F), -160.6 (m, 8F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.45 - 7.09$ (m, 40H; Ph); elemental analysis calcd (%) for $C_{72}H_{40}Au_4F_{20}P_4$: C 39.35, H 1.85; found: C 38.90, H 1.35.

Synthesis of $[Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Ag]_2$ (6): A solution of $AgClO_4$ (0.021 g, 0.1 mmol) in diethyl ether (10 mL) was added to a solution of compound **2** (0.1 g, 0.1 mmol) and PPN(acac)[31] (0.127 g, 0.2 mmol) in dichloromethane (10 mL). After 1 h of stirring the solvent was evaporated, diethyl ether (20 mL) was added and the mixture was filtered to remove the insoluble $PPN(ClO_4)$. Concentration of the solution and addition of hexane (20 mL) led to the precipitation of **6** as a pale yellow solid (0.035 g). Yield: 35%; MS ($LSIMS^+$): m/z (%): 1117 (25) $[M/2+Ag]^+$, 841 (100) $[M/2 - C_6F_5]^+$, 489 (75) $[Au(\mu\text{-}PPh_2)Ag]^+$; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 15.7$ (dm); ^{19}F NMR ($CDCl_3$): $\delta = -120.8$ (m, 8F; *o*-F), -158.9 (t, $^3J(F_p,F_m) = 20.0$ Hz, 4F; *p*-F), -160.8 (m, 8F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.49 - 7.12$ (m, 40H; Ph); elemental analysis calcd (%) for $C_{72}H_{40}Ag_2Au_2F_{20}P_4$: C 42.85, H 2.00; found: C 43.40, H 2.15.

Synthesis of $[Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Cu]_2$ (7): $[Cu(NCMe)_4]TfO$ (0.038 g, 0.1 mmol) and PPN(acac) (0.127 g, 0.2 mmol) were added to a solution of compound **2** (0.1 g, 0.1 mmol) in dichloromethane (20 mL). The resulting yellow solution was stirred for 1 h, solvent was evaporated to dryness, diethyl ether was added and the mixture was filtered to remove PPN(TfO) and $PPN(ClO_4)$, both insoluble. The resulting solution was concentrated in vacuo and cold hexane was added to afford **7** as a pale yellow solid (0.053 g). Yield: 55%; MS (ES^+): m/z (%): 1029 (35) $[M/2+Cu]^+$, 797 (75) $[M/2 - C_6F_5]^+$; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -2.7$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -120.7$ (m, 8F; *o*-F), -159.0 (t, $^3J(F_p,F_m) = 20.0$ Hz, 4F; *p*-F), -161.0 (m, 8F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.28 - 7.08$ (m, 40H; Ph); elemental analysis calcd (%) for $C_{72}H_{40}Au_2Cu_2F_{20}P_4$: C 44.80, H 2.10; found: C 44.10, H 2.30.

Synthesis of PPN[{Au(C_6F_5)$_2$(μ-PPh_2)$_2$}$_2$Cu] (8): [Cu(NCMe)$_4$]TfO (0.038 g, 0.1 mmol) and PPN(acac) (0.254 g, 0.4 mmol) were added to a solution of compound **2** (0.2 g, 0.2 mmol) in dichloromethane (20 mL). The resulting bright yellow solution was stirred for 1 h and then concentrated in vacuo. Diethyl ether was added and the mixture was filtered to remove insoluble PPN(TfO) and PPN(ClO_4). The resulting yellow solution was concentrated to ≈5 mL and hexane was added to afford **8** as a bright yellow solid (0.089 g). Yield: 37%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.1$ (s, 2P; PPN^+), −6.9 (s, 4P; PPh_2); ^{19}F NMR ($CDCl_3$): $\delta = -120.4$ (m, 8F; *o*-F), −161.9 (t, $^3J(F_p,F_m) = 20.0$ Hz, 4F; *p*-F), −162.5 (m, 8F; *m*-F); ^1H NMR ($CDCl_3$): $\delta =$ 7.65–6.84 (m, 70H; Ph); elemental analysis calcd (%) for $C_{108}H_{70}Au_2CuF_{20}NP_6$: C 53.95, H 2.95, N 0.60; found: C 54.10, H 3.40, N 0.70.

Synthesis of NBu$_4$[Au(C_6F_5)$_3$(μ-PPh_2)Au(C_6F_5)] (9): [Au(C_6F_5)(tht)] (0.090 g, 0.2 mmol) and NBu$_4$(acac) (0.068 g, 0.2 mmol) were added to a freshly prepared solution of [Au(C_6F_5)$_3$(PPh_2H)][17] (0.2 mmol) in dichloromethane (20 mL). After stirring for 1 h, the solvent was partially evaporated and hexane was added to afford **9** as a white solid (0.16 g). Yield: 54%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.2$ (s); ^{19}F NMR ($CDCl_3$): $\delta =$ −115.3 (m, 2F; *o*-F), −159.5 (t, $^3J(F_p,F_m) = 20.2$ Hz, 1F; *p*-F), −162.4 (m, 2F; *m*-F), −119.5 (m, 4F; *o*-F), −159.9 (t, $^3J(F_p,F_m) = 20.1$ Hz, 2F; *p*-F), −162.7 (m, 4F; *m*-F), −120.6 (m, 2F; *o*-F), −160.2 (t, $^3J(F_p,F_m) = 20.1$ Hz, 1F; *p*-F), −162.7 (m, 2F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.69$–7.20 (m, 10H; Ph), 3.1 (m, 8H; CH_2), 1.6 (m, 8H; CH_2), 1.4 (m, 8H; CH_2), 1.0 (t, 12H; CH_3); elemental analysis calcd (%) for $C_{52}H_{46}Au_2F_{20}NP$: C 41.90, H 3.10, N 0.95; found: C 42.55, H 3.00, N 0.85.

Synthesis of [Au(C_6F_5)$_3$(μ-PPh_2)Au(PPh_3)] (10): [Au(acac)(PPh_3)] (0.112 g, 0.2 mmol) was added to a freshly prepared solution of [Au(C_6F_5)$_3$(PPh_2H)] (0.2 mmol) in dichloromethane (20 mL). Partial evaporation of the solvent and addition of hexane led to the precipitation of **10** as a white solid (0.153 g). Yield: 57%; MS (LSIMS$^+$): *m*/*z* (%): 1342 (5) $[M]^+$; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 44.6$ (A, $AuPPh_3$), 31.1 (B, PPh_2) [J(A,B) = 297 Hz]; ^{19}F NMR ($CDCl_3$): $\delta = -119.2$ (m, 4F; *o*-F), −158.9 (t, $^3J(F_p,F_m) = 20.0$ Hz, 2F; *p*-F), −161.9 (m, 4F; *m*-F), −121.1 (m, 2F; *o*-F), −159.1 (t, $^3J(F_p,F_m) = 19.9$ H, 1F; *p*-F), −162.0 (m, 2F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.55$–7.25 (m, 25H; Ph); elemental analysis calcd (%) for $C_{48}H_{25}Au_2F_{15}P_2$: C 42.95, H 1.85; found: C 42.65, H 1.65.

Synthesis of [Au(C_6F_5)$_3$(μ-PPh_2)Ag(PPh_3)]·C_6H_{14} (11): NBu$_4$(acac) (0.068 g, 0.2 mmol) and [Ag(TfO)(PPh_3)] (0.104 g, 0.2 mmol) were added to a freshly prepared solution of [Au(C_6F_5)$_3$(PPh_2H)] (0.2 mmol) in diethyl ether (20 mL) and a white solid immediately appeared. After stirring for 1 h, the NBu$_4$(TfO) formed was filtered off, the solvent was evaporated in vacuo to ≈5 mL and cold hexane was added to obtain **11** as a white solid (0.108 g). Yield: 40%; MS (APCI$^+$): *m*/*z* (%): 1087 (90) $[M - C_6F_5]^+$; $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C): $\delta = 14.7$ (A, $AgPPh_3$), 3.2 (B, PPh_2) [J(A,B) = 158 Hz, J(A,Ag) = 541, 467 Hz]; ^{19}F NMR ($CDCl_3$): $\delta =$ −119.9 (m, 4F; *o*-F), −159.4 (t, $^3J(F_p,F_m) =$ 19.8 Hz, 2F; *p*-F), −161.8 (m, 4F; *m*-F), −121.0 (m, 2F; *o*-F), −159.2 (t, $^3J(F_p,F_m) = 20.0$ Hz, 1F; *p*-F), −162.1 (m, 2F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.52$–7.15 (m, 25H; Ph), 0.98 (t, 6H; CH_3, C_6H_{14}), 0.87 (m, 8H; CH_2, C_6H_{14}); elemental analysis calcd (%) for $C_{48}H_{25}AgAuF_{15}P_2 \cdot C_6H_{14}$: C 48.40, H 2.95; found: C 48.05, H 3.10.

Synthesis of PPN[Au(C_6F_5)$_3$(acac)] (12): Tl(acac)[33] (0.030 g, 0.1 mmol) was added to a solution of PPN[Au(C_6F_5)$_3$Cl][34] (0.127 g, 0.1 mmol) in toluene (20 mL). The mixture was stirred for 8 h at 120 °C, and the TlCl formed was filtered off. The resulting solution was concentrated to ≈5 mL and cold hexane (20 mL) was added to afford **12** as a white solid (0.091 g). Yield: 68%; MS (ES$^-$): *m*/*z* (%): 797 (10) $[M]^-$; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.1$ (s, PPN); ^{19}F NMR ($CDCl_3$): $\delta = -120.8$ (m, 4F; *o*-F), −160.5 (t, $^3J(F_p,F_m) = 20.0$ Hz, 2F; *p*-F), −163.3 (m, 4F; *m*-F), −121.8 (m, 2F; *o*-F), −160.9 (t, $^3J(F,F) = 20.0$ Hz, 1F; *p*-F), −163.2 (m, 2F; *m*-F); ^1H NMR ($CDCl_3$): $\delta = 7.64$–7.42 (m, 30H; Ph, PPN), 4.22 (s, 1H; CH), 2.09 (s, 6H; CH_3); elemental analysis calcd (%) for $C_{59}H_{37}AuF_{15}NO_2P_2$: C 53.05, H 2.80, N 1.05; found: C 53.00, H 2.65, N 1.10.

Crystallography: The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens P4 diffractometer (**6** and **10**) or a Siemens SMART 1000 CCD area detector (**11**), each equipped with a Siemens LT-2 low-temperature attachment. Data were collected with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), scan type ω (**10** and **11**) or θ–2θ (**6**). Absorption correction was carried out by ψ scans (**6** and **10**) or multiple scans (SADABS) (**11**). The structures were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 (SHELXL-93 **6** and **10**, SHELXL-97 **11**).[35] Hydrogen atoms were included by means of a riding model. Further details are given in Table 3. In compound **10**, the solvent molecule (1,1-dichloroethane) is disordered. A reasonable disorder model involved three alternative orientations with a common central C atom.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 141094–141096 (compounds **6**, **10** and **11** respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 3. Details of data collection and structure refinement for complexes **6**, **10** and **11**.

	6	**10**·$C_2H_4Cl_2$	**11**
formula	$C_{76}H_{48}Ag_2Au_2Cl_3F_{20}P_4$	$C_{50}H_{29}Au_2Cl_2F_{15}P_2$	$C_{48}H_{25}AgAuF_{15}P_2$
crystal habit	colourless prism	colourless tablet	colourless tablet
crystal size [mm]	0.35 × 0.30 × 0.20	0.40 × 0.40 × 0.15	0.45 × 0.25 × 0.18
crystal system	monoclinic	triclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
a [Å]	30.549(2)	11.706(2)	11.529(2)
b [Å]	14.0760(10)	13.841(2)	14.026(2)
c [Å]	36.7780(3)	16.298(3)	14.645(2)
α [°]	90	77.574(12)	98.258(10)
β [°]	107.559(6)	75.281(12)	100.494(10)
γ [°]	90	76.251(10)	108.411(10)
V [Å^3]	15078(15)	2447.0(7)	2157.4(6)
Z	8	2	2
ρ_{calcd} [g cm^{-3}]	1.922	1.956	1.930
M	2181.05	1441.50	1253.46
F(000)	8376	1372	1208
T [°C]	−100	−100	−130
$2\theta_{max}$ [°]	48	50	56
$\mu(Mo_{K\alpha})$ [cm^{-1}]	4.67	6.3	4.0
transmission	0.455–0.291	0.902–0.463	0.999–0.660
reflections measured	19758	9726	14579
unique reflections	11796	8528	10226
R_{int}	0.091	0.0188	0.0199
R [$F > 4\sigma(F)$][a]	0.046	0.0339	0.0296
wR [F^2, all data][b]	0.086	0.0824	0.0712
reflections used	11796	8528	10226
parameters	965	639	604
restraints	0	613	574
S[c]	1.011	0.982	1.015
max. residual electron density [e Å^{-3}]	1.755	1.796	1.551

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, 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.

[1] *Gold: Progress in Chemistry, Biochemistry and Technology* (Ed.: H. Schmidbaur), Wiley, Chichester, **1999**.

[2] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.

[3] a) P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563; b) P. Pyykkö,Y. F. Zhao, *Angew. Chem.* **1991**, *103*, 622; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 604; c) J. Li, P. Pyykkö, *Chem. Phys. Letters* **1992**, *197*, 586; d) J. Li, P. Pyykkö, *Inorg. Chem.* **1993**, *32*, 2630; e) P. Pyykkö, N. Runeberg, F. Mendizabal, *Chem. Eur. J.* **1997**, *3*, 1451; f) P. Pyykkö, F. Mendizabal, *Inorg. Chem.* **1998**, *37*, 3018; g) E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. A. Rodríguez, O. Crespo, M. C. Gimeno, A. Laguna, P. G. Jones, *Inorg. Chem.* **1998**, *37*, 6002.

[4] a) H. Schmidbaur, *Gold Bull.* **1990**, *23*, 11; b) H. Schmidbaur, *Interdiscip. Sci. Rev.* **1992**, *7*, 213; c) H. Schmidbaur, *Pure Appl. Chem.* **1993**, *65*, 691; d) H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 391; e) M. Bardají, A. Laguna, *J. Chem. Ed.* **1999**, *76*, 201.

[5] P. J. Sadler, R. E. Sue, *Met. Based Drugs* **1994**, *1*, 107.

[6] a) S. Wang, G. Garzón, C. King, J. C. Wang, J. P. Fackler, Jr., *Inorg. Chem.* **1989**, *28*, 4623; b) R. Narayanaswamy, M. A. Young, E. Parkhust, M. Ouellette, M. E. Kerr, D. M. Ho, R. C. Elder, A. E. Bruce, M. R. M. Bruce, *Inorg. Chem.* **1993**, *32*, 2506; c) S. S. Tang, C. P. Chang, I. J. B. Lin, L. S. Liou, J. C. Wang, *Inorg. Chem.* **1997**, *36*, 2294.

[7] a) M. Bardají, A. Laguna, V. M. Orera, M. D. Villacampa, *Inorg. Chem.* **1998**, *37*, 5125; b) E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, M. C. Gimeno, A. Laguna, P. G. Jones, *Inorg. Chem.* **1998**, *37*, 5532 and references cited therein.

[8] a) R. Usón, A. Laguna, M. V. Castrillo, *Synth. React. Inorg. Met. Org. Chem.* **1979**, *9*, 317; b) H. Schmidbaur, A. A. M. Aly, U. Schubert, *Angew. Chem.* **1978**, *90*, 905; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 846; c) S. Canales, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, *Chem. Commun.* **1999**, 679; d) O. Crespo, F. Canales, M. C. Gimeno, P. G. Jones, A. Laguna, *Organometallics* **1999**, *18*, 3142; e) "Aurophilicity at Chalcogenide Centers. Synthesis of Polynuclear Chalcogenido-Centered Complexes with Gold–Gold Interactions", O. Crespo, M. C. Gimeno, A. Laguna in *Metal Clusters in Chemistry*, *Vol. 1* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**, p. 477 and references cited therein.

[9] H. Schmidbaur, A. Grohmann, M. E. Olmos in *Gold: Progress in Chemistry, Biochemistry and Technology*, (Ed.: H. Schmidbaur), Wiley, Chichester, **1999**, p. 647.

[10] a) F. Canales, M. C. Gimeno, A. Laguna, P. G. Jones, *Organometallics* **1996**, *15*, 3412; b) M. C. Blanco, E. J. Fernández, A. Fischer, P. G. Jones, A. Laguna, M. E. Olmos, M. D. Villacampa, *Inorg. Chem. Commun.* **2000**, *3*, 163.

[11] a) S. Doherty, M. Waugh, T. H. Scanlan, M. R. J. Elsegood, W. Clegg, *Organometallics* **1999**, *18*, 679; b) P. Blenkiron, J. F. Corrigan, N. J. Taylor, A. J. Carty, *Organometallics* **1997**, *16*, 297; c) B. F. G. Johnson, J. Lewis, E. Nordlander, P. R. Raithby, C. E. Housecroft, *Inorg. Chim. Acta* **1997**, *259*, 345.

[12] a) G. A. Acum, M. J. Mays, P. R. Raithby, H. R. Powel, G. A. Solan, *J. Chem. Soc. Dalton Trans.* **1997**, 3427; b) K. Wang, T. J. Emge, A. S. Goldman, *Inorg. Chim. Acta* **1997**, *255*, 395.

[13] a) P. Leoni, G. Chiaradonna, M. Pasquali, F. Marchetti, *Inorg. Chem.* **1999**, *38*, 253; b) E. Alonso, J. Forniés, C. Fortuño, A. Martín, G. M. Rosair, A. J. Welch, *Inorg. Chem.* **1997**, *36*, 4426.

[14] R. J. Puddephatt, P. J. Thompson, *J. Organomet. Chem.* **1976**, *117*, 395.

[15] a) R. G. Pritchard, D. B. Dyson, R. V. Parish, C. A. McAuliffe, B. Beagley, *J. Chem. Soc. Chem. Commun.* **1987**, 371; b) D. B. Dyson, R. V. Parish, C. A. McAuliffe, R. G. Pritchard, R. Fields, B. Beagley, *J. Chem. Soc. Dalton Trans.* **1989**, 907; c) H. Schmidbaur, A. A. M. Aly, *Z. Naturforsch. Teil B* **1979**, *34*, 23; d) H. Schmidbaur, G. Weidenhiller, A. A. M. Aly, O. Steigelmann, G. Müller, *Z. Naturforsch. Teil B* **1989**, *44*, 1503.

[16] a) J. Vicente, M. T. Chicote, P. G. Jones, *Inorg. Chem.* **1993**, *32*, 4960; b) G. A. Carriedo, V. Riera, M. L. Rodríguez, P. G. Jones, J. Lautner, *J. Chem. Soc. Dalton Trans.* **1989**, 639; c) F. S. Livotto, M. D. Vargas, D. Braga, F. Grepioni, *J. Chem. Soc. Dalton Trans.* **1992**, 577.

[17] M. C. Blanco, E. J. Fernández, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, M. E. Olmos, *Angew. Chem.* **1998**, *110*, 3199; *Angew. Chem. Int. Ed.* **1998**, *37*, 3042.

[18] R. Usón, A. Laguna, *Coord. Chem. Rev.* **1986**, *70,* 1.

[19] B. J. Hathaway, A. E. Underhill, *J. Chem. Soc.* **1961**, 3091.

[20] E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna, J. M. López-de-Luzuriaga, *Organometallics*, **1995**, *14*, 2918.

[21] B. Alvarez, E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna, J. M. López-de-Luzuriaga, *J. Organomet. Chem.* **1996**, *525*, 109

[22] E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, M. E. Olmos, *Chem. Ber.* **1997**, *130*, 1513.

[23] C. W. Liu, H. Pau, J. P. Fackler, Jr., G. Wu, R. E. Wasylishen, M. Shang, *J. Chem. Soc. Dalton Trans.* **1995**, 3691.

[24] See for example: a) R. Usón, J. Forniés, *Inorg. Chim. Acta.* **1992**, *198–200*, 165; b) J. M. Casas, L. R. Falvello, J. Forniés, A. Martín, *Inorg. Chem.* **1996**, *35*, 7867; c) J. Forniés, A. Martín in *Metal Custers in Chemistry*, *Vol. 1* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**, p. 417.

[25] J. Vicente, M. T. Chicote, I. Saura-Llamas, M. C. Lagunas, M. C. Ramírez de Arellano, P. González-Herrero, M. D. Abrisqueta, R. Guerrero in *Metal Clusters in Chemistry*, *Vol. 1* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**, p. 493.

[26] K. Nakamoto in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, Chichester, **1986**, p. 264.

[27] G. J. Kubas, *Inorg. Synth.* **1990**, *28*, 68.

[28] R. Usón, A. Laguna, *Inorg. Synth.* **1982**, *21*, 71.

[29] R. Usón, A. Laguna, J. Vicente, *J. Chem. Soc. Chem. Commun.* **1976**, 353.

[30] R. Usón, A. Laguna, M. L. Arrese, *Synth. React. Inorg. Met. Org. Chem*. **1984**, *14*, 557.

[31] E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna, J. M. López-de-Luzuriaga, *J Chem. Soc. Dalton Trans.* **1992**, 3365.

[32] E. G. Perevalova, E. I. Smyslova, V. P. Dyadchenko, K. I. Grandberg, A. N. Nesmeyanov, *Izv. Akad. Nauk. SSSR Ser. Khim.* **1980**, 1455.

[33] J. Vicente, M. T. Chicote, *Inorg. Synth.* **1998**, *32*, 172.

[34] R. Usón, A. Laguna, M. Laguna, E. J. Fernández, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc. Dalton Trans.* **1982**, 1971.

[35] G. M. Sheldrick, *SHELXL-97, A Program for Crystal Structure Refinement*, University of Göttingen, **1993** or **1997**.

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