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Gold(III) Phenylphosphides and -phosphodiides

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In this paper we describe the synthesis of a series of cyclic and acyclic gold phosphine, phosphide, and phosphodiide derivatives of the primary phosphine $PPhH_2$. Thus, by reacting $[Au(C_6F_5)_x(tht)]$ ($x = 1, 3$) with an equimolecular amount of $PPhH_2$, the phosphino complexes $[Au(C_6F_5)_x(PPhH_2)]$ ($x = 1, 3$) are obtained. The gold(III) complex $[Au(C_6F_5)_3(PPhH_2)]$ reacts with gold(I), silver(I), or gold(III) reagents in the presence of a deprotonating agent, leading to the new di- or trinuclear phenylphosphide derivatives $[Au(C_6F_5)_3(\mu\text{-}PPhH)Au(PR_3)]$ (R = Ph, Me), $PPN[\{Au(C_6F_5)_3\}_2(\mu\text{-}PPhH)]$, or $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPhH)\}_2M]$ (M = Au, Ag). The anionic gold(III) complex $PPN[\{Au(C_6F_5)_3\}_2(\mu\text{-}PPhH)]$ further reacts with similar gold(I) precursors to afford higher nuclearity phosphodiide species, such as $PPN[\{Au(C_6F_5)_3\}_2(\mu_3\text{-}PPh)\{Au(PPh_3)\}]$, $(PPN)_2[\{Au(C_6F_5)_3\}_2(\mu_3\text{-}PPh)\{Au(C_6F_5)\}]$, or $(PPN)_3[\{(Au(C_6F_5)_3)_2(\mu_3\text{-}PPh)\}_2Au]$. Furthermore, treatment of $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$ with $PPhH_2$ results in the formation of the cyclic trinuclear complex $[Au(C_6F_5)_2(\mu\text{-}PPhH)]_3$, which can further react with $[Au(acac)(PPh_3)]$ to afford the tetranuclear phosphide/phosphodiide derivative $[\{Au(C_6F_5)_2(\mu\text{-}PPhH)\}_2\{Au(C_6F_5)_2(\mu_3\text{-}PPh)Au(PPh_3)\}]$. The crystal structures of compounds $PPN[\{Au(C_6F_5)_3\}_2(\mu\text{-}PPhH)]$, $[\{Au(C_6F_5)_3\}(\mu_3\text{-}PPh)\{Au(PPh_3)\}_2]$, and $[Au(C_6F_5)_2(\mu\text{-}PPhH)]_3$ have been determined by X-ray diffraction methods.

Introduction

During the past few years, various research groups have contributed to the development of the chemistry of phosphido complexes of main group[1−3] or transition[4−6] metals, with phosphido ligands that bridge metal centers. There is a great number of compounds of this type containing metals mainly of groups 6[7−12] or 10,[13−20] whereas the number of gold phosphides is much lower, despite the great attention that the synthesis of di- and polynuclear phosphido-bridged complexes attracts because of their possible catalytic behavior.[21]

Thus, when we started our research work in this field, only a few gold(I) species containing secondary phosphines[22−25] or their phosphido derivatives[23,24,26,27] were known. In the case of primary phosphines, the gold(I) chemistry was even more limited, with the sole contributions being by Schmidbaur, who described species of the type $[AuX(PRH_2)]$[28] or tri- and tetraaurated phosphonium salts.[29] Moreover, the chemistry of both primary and secondary phosphines or their phosphides was

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almost nonexistent for gold(III), with the only example being the dinuclear derivative $[\mathrm{Au_2Me_4}(\mu\text{-}\mathrm{PPh_2})_2]$.[26] This was also the only organometallic gold derivative with this type of ligand at the time.

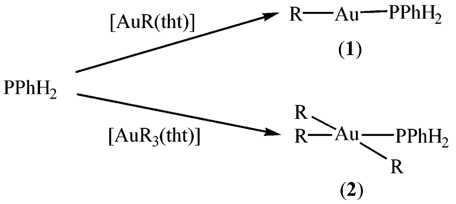
We have recently reported the synthesis and reactivity of a number of organogold(III) phosphino- and phosphido-bridged derivatives of the secondary phosphine $\mathrm{PPh_2H}$, containing gold(III) or gold(III) and M(I) (M = Cu, Ag, Au) centers.[30]

To increase the nuclearity of the products, we decided to extend this study to the primary phosphine $\mathrm{PPhH_2}$, which contains two (instead of only one) hydrogen atoms that could be substituted by a metal atom. We have now succeeded in synthesizing the first gold(III) complexes with a primary phosphine ($\mathrm{PRH_2}$) or its deprotonated forms $\mathrm{PRH^-}$ or $\mathrm{PR^{2-}}$ as ligands. Thus, in this paper we describe a series of compounds with phenylphosphine, phenylphosphide, and even phenylphosphodiide ligands bonded to gold(III), or bridging gold(III) or gold(III) and gold(I) centers.

Results and Discussion

Phosphino Complexes. The phenylphosphinegold complexes $[\mathrm{Au(C_6F_5)}_x(\mathrm{PPhH_2})]$ ($x = 1$ (**1**), 3 (**2**)) have been obtained by displacement of the weakly coordinated ligand tetrahydrothiophene from $[\mathrm{Au(C_6F_5)}_x(\mathrm{tht})]$ when treated with the free phosphine in equimolecular amounts (see Scheme 1). Complexes **1** and **2** are isolated as moderately air- and moisture-stable white solids, soluble in chlorinated solvents and acetone, partially soluble in diethyl ether, and insoluble in hexane. The gold(I) species **1** is less stable in solution, and autodeprotonation to form $\mathrm{C_6F_5H}$, as previously reported in other cases,[31] is observed after some minutes.

Scheme 1[a]



[a] R = $\mathrm{C_6F_5}$.

Both complexes are nonconducting in acetone solutions. Their IR spectra show the absorptions from a pentafluorophenyl group bonded to gold(I) at 1501 (vs), 950 (vs), and 789 $\mathrm{cm^{-1}}$ (s, br) or from a tris(pentafluorophenyl)gold(III) fragment[32] at 1506 (vs), 966 (vs), and 794 $\mathrm{cm^{-1}}$ (s, br). In their mass spectra (ES) the molecular peak appears as the parent peak at $m/z = 473$ (**1**) or 807 (**2**).

Their $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra display a broad singlet (because of the coupling of the phosphorus atom with *trans* fluorine atoms) at −46.0 (**1**) and −59.3 ppm (**2**), shifted to low field relative to the signal of the free ligand at −122.2 ppm, and the $^{19}\mathrm{F}$ NMR spectra show the three typical groups of resonances of $\mathrm{Au(C_6F_5)}$ or $\mathrm{Au(C_6F_5)_3}$ fragments for **1** or **2**, respectively. Furthermore, their $^1\mathrm{H}$ NMR spectra display one doublet at 6.15 [$J_{\mathrm{P-H}} = 376$ Hz] (**1**) or 5.92 ppm [$J_{\mathrm{P-H}} = 414$ Hz] (**2**) for the nonaromatic protons.

Phosphide Complexes. As commented above, we are interested not only in the synthesis of phenylphosphine derivatives but also in their utilization as starting materials for the further preparation of polynuclear phosphido-bridged compounds. Thus, complex **2** was treated with equimolecular amounts of $[\mathrm{Au(acac)(PPh_3)}]$ or $[\mathrm{AuCl(PMe_3)}]$ and Tl(acac), reactions that lead to the dinuclear neutral derivatives $[\mathrm{Au(C_6F_5)_3}(\mu\text{-}\mathrm{PPhH})\mathrm{Au(PR_3)}]$ (R = Ph (**3**), Me (**4**)), in which a gold(I) fragment has been incorporated. They are obtained as air- and moisture-stable white solids that are nonconducting in acetone solutions. Their IR spectra show the three bands typical of tris(pentafluorophenyl) compounds at $\nu = 1505$ (vs), 967 (vs), and 793 (s, br).

In their $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra an AX system (as a consequence of the coupling of the nonequivalent phosphorus atoms of the phosphine and phenylphosphide ligands) is observed. The substitution of a proton for a metallic fragment produces a shift to low field, and consequently, the phosphorus of the phosphide ligand appears at −31.6 (**3**) or −32.7 ppm (**4**), while the phosphorus of the tertiary phosphine is located at 45.1

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Table 1. Details of Data Collection and Structure Refinement for Complexes 5, 8, and 13

	5	**8**	**13**
chemical formula	$C_{70}H_{36}Au_2F_{30}NP_3$	$C_{60}H_{35}Au_3F_{15}P_3 \cdot CHCl_3$	$C_{54}H_{18}Au_3F_{30}P_3 \cdot 0.25CH_2Cl_2$
cryst habit	colorless tablet	colorless tablet	colorless plate
cryst size/mm	0.26 × 0.24 × 0.12	0.32 × 0.28 × 0.2	0.25 × 0.15 × 0.10
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/n$
a/Å	13.1839(12)	23.9558(18)	14.3742(2)
b/Å	17.2921(14)	20.5905(16)	21.4249(3)
c/Å	18.2913(16)	26.249(2)	19.2234(3)
α/deg	99.841(3)	90	90
β/deg	105.470(3)	110.268(3)	102.683(1)
γ/deg	109.980(3)	90	90
V/Å^3	3615.5(5)	12145.9(16)	5775.70(15)
Z	2	8	4
D_c/g cm^{-3}	1.877	2.017	2.243
M	2043.92	1844.06	1950.34
F(000)	1968	6960	3634
T/°C	−130	−130	−100
$2\theta_{max}$/deg	60	60	56
μ(Mo Kα)/mm^{-1}	4.244	7.526	7.855
transmission	0.923−0.692	0.928−0.721	0.507−0.244
no. of reflns measd	76 853	119 658	44 891
no. of unique reflns	21 110	17 768	13 655
R_{int}	0.0318	0.0458	0.0607
R [$F > 2\sigma(F)$]^a	0.0224	0.0239	0.0473
wR [F^2, all reflns]^b	0.0512	0.0565	0.1134
no. of reflns used	21 110	17 768	13 655
no. of params	1026	792	841
no. of restraints	992	743	348
S^c	0.963	0.971	1.021
max. residual electron density/e Å^{-3}	1.441	1.454	1.884

[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.

(**3**) or 8.3 ppm (**4**). Complexes **3** and **4** are chiral, but by NMR spectrometry it is not distinguishable if they are obtained as racemic or more complex mixtures. Their ^{19}F NMR spectra show again three groups of resonances (in a 2:1 ratio) from the *ortho*, *meta*, and *para* fluorine atoms of the pentafluorophenyl groups bonded to gold(III), and their ^{1}H NMR spectra show the doublet from the nonaromatic hydrogen of the phenylphosphide ligand centered at 5.79 (**3**) or 5.65 ppm (**4**). In the case of **4** a doublet associated with the methyl protons of PMe_3 is also observed at 1.65 ppm [J_{P-H} = 9.6 Hz].

To incorporate a second gold(III) center, the reaction of complex **2** with an equimolecular amount of $[Au(C_6F_5)_3(tht)]$ in the presence of PPN(acac) was carried out, leading to the dinuclear anionic compound PPN$[\{Au(C_6F_5)_3\}_2(\mu\text{-}PPhH)]$ (**5**), which contains two gold(III) centers bridged only by the phosphorus atom of the phenylphosphide ligand. Complex **5** is isolated as an air- and moisture-stable white solid that behaves as a uni-univalent electrolyte in acetone solution.

In its IR spectrum, in addition to the characteristic bands of C_6F_5 groups bonded to gold(III), an absorption at 534 cm^{-1}, associated with the cation PPN$^+$, is observed. The substitution of a hydrogen atom for the second gold(III) fragment is confirmed in its ^{31}P{^{1}H} NMR spectrum, in which the singlet due to the phosphorus of the phosphide ligand is shifted to low field relative to **2**, appearing at −46.4 ppm. Its ^{19}F NMR spectrum is similar to those described for complexes **2**−**4**, and in its ^{1}H NMR spectrum a doublet from the proton bonded to phosphorus is observed at 5.32 ppm [J_{H-P} = 368 Hz]. As in complexes **1** and **2**, its mass spectrum displays the molecular ion as the parent peak at m/z = 1505.

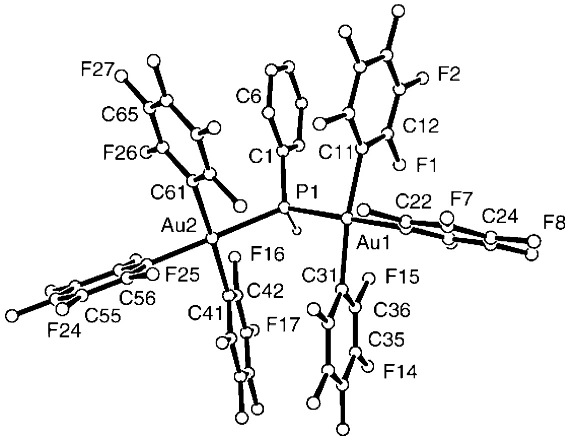
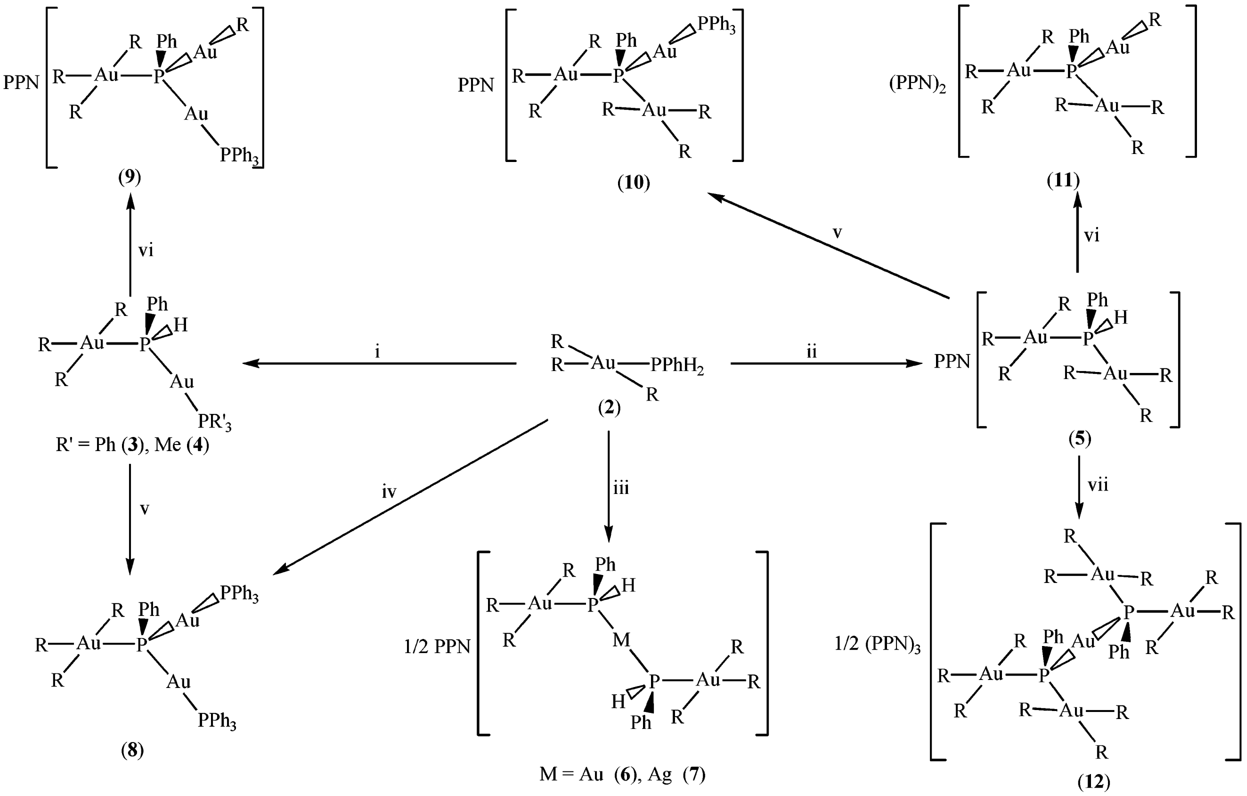


Figure 1. Structure of the anion of complex **5**. Hydrogen atoms, except the nonaromatic proton of PPhH$^-$, have been omitted for clarity. Radii are arbitrary.

Finally, the structure of **5** was determined by single-crystal X-ray diffraction from crystals obtained by layering a solution of **5** in chloroform with hexane. Compound **5** crystallizes in the triclinic system. In the anion (Figure 1) two "$Au(C_6F_5)_3$" units are bridged by the phosphide PPhH$^-$. The two gold atoms show almost perfect square-planar geometries. No Au···Au contact is present in the molecule; the distance between the two gold centers is 4.067 Å. The Au−C distances (2.058(2)−2.074(2) Å, see Table 2) are in the range found for analogous gold complexes that contain phosphide bridges, such as $[Au(C_6F_5)_3(\mu\text{-}PPh_2)M(PPh_3)]$[30c] (M = Au, 2.055(6)−2.074(6) Å; M = Ag, 2.063(3)−2.073(3) Å) or PPN$[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2M]$[30a] (2.052(5)−2.078(5) Å); a wider range of distances is found in PPN$[\{Au(C_6F_5)_3\}_2(\mu$-

Scheme 2[a]



[a] R = C_6F_5. Key: (i) [Au(acac)(PPh_3)] or [AuCl(PMe_3)] + Tl(acac); (ii) [Au(C_6F_5)$_3$(tht)] + PPN(acac); (iii) 1/2 PPN[Au(acac)$_2$] or 1/2 Ag($OClO_3$) + PPN(acac); (iv) 2 [Au(acac)(PPh_3)]; (v) [Au(acac)(PPh_3)]; (vi) [Au(C_6F_5)(tht)] + PPN(acac); (vii) 1/2 PPN[Au(acac)$_2$].

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 5

Au(1)−C(21)	2.063(2)	Au(2)−C(61)	2.064(2)
Au(1)−C(11)	2.062(2)	Au(2)−P(1)	2.3553(6)
Au(1)−C(31)	2.074(2)	P(1)−C(1)	1.815(2)
Au(1)−P(1)	2.3545(6)	P(2)−N	1.5798(19)
Au(2)−C(51)	2.058(2)		
Au(2)−C(41)	2.062(2)		
C(21)−Au(1)−C(11)	87.81(8)	C(41)−Au(2)−C(61)	176.64(8)
C(21)−Au(1)−C(31)	90.63(8)	C(51)−Au(2)−P(1)	176.11(6)
C(11)−Au(1)−C(31)	169.65(8)	C(41)−Au(2)−P(1)	89.75(6)
C(21)−Au(1)−P(1)	178.71(6)	C(61)−Au(2)−P(1)	92.78(6)
C(11)−Au(1)−P(1)	91.59(6)	C(1)−P(1)−Au(1)	112.45(8)
C(31)−Au(1)−P(1)	89.75(6)	C(1)−P(1)−Au(2)	114.32(8)
C(51)−Au(2)−C(41)	88.65(9)	Au(1)−P(1)−Au(2)	119.41(2)
C(51)−Au(2)−C(61)	88.96(9)		

PPh_2)].[30b] The Au−P distances (2.3545(6), 2.3553(6) Å) are shorter than the Au(III)−P bond lengths found in [Au(C_6F_5)$_3$(μ-PPh_2)M(PPh_3)] (M = Au, 2.3734(17) Å; M = Ag, 2.3821(9) Å) or PPN[{Au(C_6F_5)$_3$(μ-PPh_2)}$_2$M] (M = Ag, Au; 2.365 Å in both complexes).

To increase the nuclearity of the products, we treated complex **2** with PPN[Au(acac)$_2$] (2:1) or with Ag($OClO_3$) and PPN(acac) (2:1:2), reactions that lead to the extraction of one hydrogen from each molecule of **2** and to the coordination of two $PPhH^-$ ligands to the new metallic center (see Scheme 2), affording the trinuclear mixed Au^{III}−M^I compounds PPN[{Au(C_6F_5)$_3$(μ-PPhH)}$_2$M] (M = Au (**6**), Ag (**7**)). They are obtained as stable white solids that behave as 1:1 electrolytes in acetone solution.

The absorptions characteristic of tris(pentafluorophenyl)gold compounds are observed in their IR spectra, as well as a band at $\nu = 532$ cm^{-1} from the cation PPN^+. In their $^{31}P\{^1H\}$ NMR spectra, apart from the singlet corresponding to the phosphorus of the cation, two signals located at −31.0 and −33.3 (**6**) or at −66.3 and −69.3 ppm (**7**) can be observed. The presence of two instead of one resonance for the equivalent phosphide groups is associated with the presence of two diastereoisomer pairs, arising from the chirality of both phosphorus atoms in these complexes. Related stereoisomerism having its origin in the rotation about the P−C bonds (which is in this case temperature dependent) has also been observed in other complexes of the type [R_3P−M−PR_3]$^+$ (M = Cu, Ag, Au).[33] In addition, in the case of the silver derivative **7** each signal splits into two doublets at 223 K as a consequence of the coupling of the phosphorus atoms with the magnetically active ^{107}Ag and ^{109}Ag isotopes.

Their ^{19}F and ^1H NMR spectra also show the presence of different isomers displaying twice as many resonances as the phenylphosphide complexes described above. In their ^1H NMR spectra, although the A part of a AXX′A′ spin system could have been expected, a more simple system only showing two doublets centered at 5.70 and 5.53 (**6**) or 4.80 and 4.66 ppm (**7**) is observed. Finally, their mass spectra (ES−) display the molecular anion as the parent peak at *m*/*z* = 1811 (**6**) or 1723 (**7**) with experimental isotopic distributions in agreement with the calculated ones.

Phosphodiide Complexes. When the reaction between **2** and [Au(acac)(PPh_3)] is carried out in a 1:2 molar ratio, each hydrogen atom of phenylphosphine is replaced with a triphenylphosphinegold(I) fragment,

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[33] Bayler, A.; Bowmaker, G. A.; Schmidbaur, H. *Inorg. Chem.* **1996**, *35*, 5959.

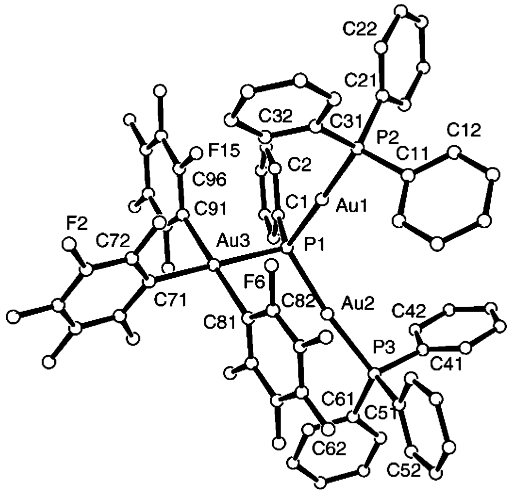

Figure 2. Molecular structure of complex **8**. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

affording the first gold(III) phosphodiide complex, $[Au(C_6F_5)_3(\mu_3\text{-}PPh)\{Au(PPh_3)\}_2]$ (**8**). The same species can also be obtained by reaction of the phosphide complex **3** with 1 equiv of $[Au(acac)(PPh_3)]$. Complex **8** is isolated as a white solid that is air- and moisture-stable at room temperature with analytical and spectroscopic data in accordance with the proposed stoichiometry.

Its IR spectrum is very similar to that registered for complex **3**. The presence of two $Au(PPh_3)$ groups is confirmed in its $^{31}P\{^1H\}$ NMR spectrum, which displays an AX_2 system instead of the AX system observed for **3**, which presents only one gold(I) fragment. The substitution of the second proton produces a greater shift to low field than in the case of **3**, and thus, the phosphorus of the PPh^{2-} ligand is located at 1.1 ppm. Its ^{19}F NMR spectrum is similar to those described above for complexes **2**–**7**, and its ^1H NMR spectrum also confirms the absence of hydrogen atoms bonded to phosphorus, showing only the resonances from the aromatic protons.

By slow diffusion of hexane into a solution of **8** in chloroform, single crystals suitable for X-ray diffraction studies were obtained. In the molecule (Figure 2), one phosphodiide ligand $[PPh]^{2-}$ bridges two gold(I) and one gold(III) atom. The gold(I) centers exhibit distorted linear geometries (P–Au–P angles 178.97(3)°, 173.37(3)°, see Table 3). The gold(III) atom displays an almost perfect square-planar environment. The Au(I)···Au(I) or Au(I)···Au(III) distances are all longer than 3.6 Å. The Au(I)–P distances (2.2982(8)–2.3213(8) Å) compare well with those found in $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2Au]$[30a] (2.319(2) Å) or $PPN[Mn(CO)_4(\mu\text{-}PPh_2)Au(C_6F_5)_2]$[34] (2.313(2)–2.322(1) Å). The Au(III)–P distance (2.3603(8) Å) is longer than those in **5**. The Au–C distances (2.055(3)–2.083(3) Å) are in the range found for **5**.

In view of these results, and in order to synthesize a new type of complex that contained three different metallic fragments bridged by the phenylphosphodiide ligand, we treated **3** with equimolecular amounts of $[Au(C_6F_5)(tht)]$ and PPN(acac), a reaction that leads to the anionic trinuclear species $PPN[Au(C_6F_5)_3(\mu_3\text{-}PPh)\{Au(PPh_3)\}\{Au(C_6F_5)\}]$ (**9**). This too is obtained as a white stable solid that behaves as a 1:1 electrolyte in acetone solution.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 8

Au(1)–P(2)	2.3011(8)	P(1)–C(1)	1.825(3)
Au(1)–P(1)	2.3190(8)	P(2)–C(31)	1.806(3)
Au(2)–P(3)	2.2982(8)	P(2)–C(21)	1.813(4)
Au(2)–P(1)	2.3213(8)	P(2)–C(11)	1.821(3)
Au(3)–C(91)	2.055(3)	P(3)–C(61)	1.805(3)
Au(3)–C(81)	2.074(3)	P(3)–C(51)	1.813(3)
Au(3)–C(71)	2.083(3)	P(3)–C(41)	1.822(3)
Au(3)–P(1)	2.3603(8)		
P(2)–Au(1)–P(1)	178.97(3)	Au(2)–P(1)–Au(3)	110.83(3)
P(3)–Au(2)–P(1)	173.37(3)	C(31)–P(2)–C(21)	107.78(17)
C(91)–Au(3)–C(81)	177.74(12)	C(31)–P(2)–C(11)	102.63(14)
C(91)–Au(3)–C(71)	90.73(11)	C(21)–P(2)–C(11)	106.59(16)
C(81)–Au(3)–C(71)	91.01(11)	C(31)–P(2)–Au(1)	113.24(12)
C(91)–Au(3)–P(1)	91.27(8)	C(21)–P(2)–Au(1)	111.40(11)
C(81)–Au(3)–P(1)	87.04(8)	C(11)–P(2)–Au(1)	114.55(11)
C(71)–Au(3)–P(1)	177.25(9)	C(61)–P(3)–C(51)	105.97(15)
C(1)–P(1)–Au(1)	109.39(11)	C(61)–P(3)–C(41)	106.16(14)
C(1)–P(1)–Au(2)	110.11(11)	C(51)–P(3)–C(41)	104.51(14)
Au(1)–P(1)–Au(2)	113.96(3)	C(61)–P(3)–Au(2)	118.79(11)
C(1)–P(1)–Au(3)	110.53(10)	C(51)–P(3)–Au(2)	113.46(10)
Au(1)–P(1)–Au(3)	101.75(3)	C(41)–P(3)–Au(2)	106.82(10)

Its IR spectrum confirms the presence of the cation and also shows absorptions from pentafluorophenyl groups bonded to gold(I) and to gold(III). The $^{31}P\{^1H\}$ NMR spectrum displays an AX system in which the resonance corresponding to the phosphodiide ligand appears at 7.0 ppm, shifted to lower field than in the spectrum of the starting compound **3**. Complex **9** is chiral, but by NMR spectrometry it is not distinguishable if it is obtained as a racemic or a more complex mixture. In its ^{19}F NMR, besides the signals due to the $Au(C_6F_5)_3$ unit, three new resonances corresponding to the pentafluorophenyl group bonded to gold(I) can be observed. Finally, the molecular ion of **9** is detected in its mass spectrum (ES–) at $m/z = 1629$ (95%).

Complex **5** still has a hydrogen atom that can be replaced with other metallic fragments, such as $Au(PPh_3)^+$ or $Au(C_6F_5)$, to obtain phosphodiide species. Thus, it reacts with equimolecular amounts of $[Au(acac)(PPh_3)]$ or $[Au(C_6F_5)(tht)]$ and PPN(acac) to afford the trinuclear anionic complexes $PPN[\{Au(C_6F_5)_3\}_2(\mu_3\text{-}PPh)\{Au(PPh_3)\}]$ (**10**) or $(PPN)_2[\{Au(C_6F_5)_3\}_2(\mu_3\text{-}PPh)\{Au(C_6F_5)\}]$ (**11**) as white solids. Their physical and spectroscopic properties are again in accordance with the proposed stoichiometry, showing a value of 108 (**10**) or 191 Ω^{-1} cm^2 mol^{-1} (**11**) for their molar conductivity in acetone solutions.

In their IR spectra the bands associated with PPN^+ and tris(pentafluorophenyl)gold complexes can be observed, and in the case of complex **11** an absorption assigned to the C_6F_5 group bonded to gold(I) at 962 cm^{-1} (vs) also appears. Their $^{31}P\{^1H\}$ NMR spectra display, besides a singlet at 21.1 ppm due to PPN, an AX system (**10**) or a singlet (**11**), from the phosphorus atoms of the anion. The resonance due to the phosphodiide phosphorus appears at −8.7 (**10**) or −1.4 ppm (**11**), while the phosphorus of triphenylphosphine is located at 42.6 ppm in **10**. Once again, their ^{19}F and ^1H NMR spectra confirm the presence of C_6F_5 groups bonded to gold(III) (**10**) or gold(III) and gold(I) (**11**) and the absence of nonaromatic protons.

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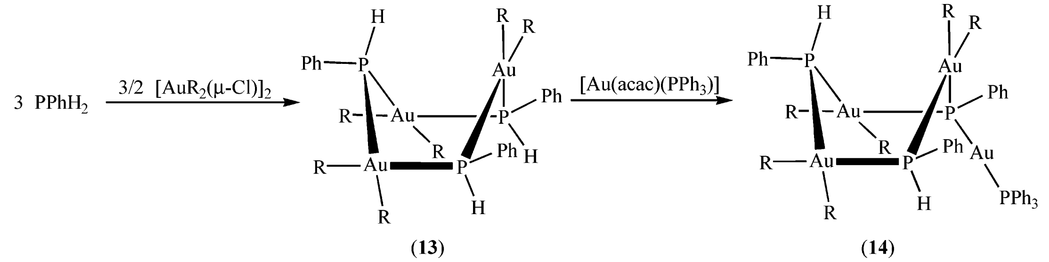
Scheme 3[a]



[a] R = C_6F_5.

In view of these results, we thought of synthesizing a higher nuclearity species by reacting the same substrate **5** with PPN[Au(acac)$_2$] in a 2:1 molar ratio. This reaction led to the pentanuclear complex (PPN)$_3$[{(Au(C$_6$F$_5$)$_3$)$_2$(μ_3-PPh)}$_2$Au] (**12**), in which the trianionic complex contains two phenylphosphodiide ligands bridging four gold(III) and one gold(I) atom. Compound **12** is isolated as a white solid soluble in most common organic solvents, but insoluble in hexane. Its molar conductivity has a value of 284 Ω^{-1} cm^2 mol^{-1}, typical of 1:3 electrolytes,[35] in accordance with the proposed stoichiometry.

Its $^{31}P\{^1H\}$ NMR spectrum displays one singlet corresponding to the phosphorus atoms of the two equivalent bridging PPh^{2-} ligands at -12.8 ppm, as well as a second singlet at 21.1 ppm from the phosphorus of the cation. Complex **12** presents a very complicated ^{19}F NMR spectrum, in which only signals corresponding to fluorine atoms of pentafluorophenyl groups bonded to gold(III) are observed. Finally, its ^1H NMR spectrum confirms the nonexistence of H$-$P bonds, displaying only signals assigned to phenyl groups.

Cyclic Complexes. We have previously reported that the reaction of PPh_2H with the chloro-bridged complex [Au(C$_6$F$_5$)$_2$(μ-Cl)]$_2$ leads to the synthesis of the phosphino or the phosphido complexes [Au(C$_6$F$_5$)$_2$Cl(PPh$_2$H)] or [Au(C$_6$F$_5$)$_2$(μ-PPh$_2$)]$_2$ depending on the molar ratio and the solvent employed in the reaction.[30b] In contrast, when the same reaction is carried out with the primary phosphine $PPhH_2$, the result is always the same, independent of the molar ratio and the solvent. In this reaction the chlorine atoms act as deprotonating agents, extracting one of the hydrogen atoms of the phosphine and promoting the formation of the cyclic trinuclear complex [Au(C$_6$F$_5$)$_2$(μ-PPhH)]$_3$ (**13**), which presents a six-membered ring formed by alternating gold(III) and phosphorus atoms (see Scheme 3). Although the same disposition of ligands and metals was found about twenty years ago in the amido derivative [Au(CH$_3$)$_2$(NH$_2$)]$_3$[36] and it has also been recently observed in the gold(I) phosphide complex [Au(PIs$_2$)]$_3$ (Is = 2,4,6-(^{i}Pr)$_3$C$_6$H$_2$),[37] such an arrangement has no precedent in the chemistry of gold(III) phosphides. This complex is obtained as an air- and moisture-stable pale yellow solid that is a nonconductor in acetone solution.

Its IR spectrum shows absorptions corresponding to pentafluorophenyl groups bonded to gold(III) in a *cis* disposition[38] at 1509 (vs), 969 (vs), and 800 (m, br). Its $^{31}P\{^1H\}$ NMR displays two singlets with different intensity located at -22.0 and -12.0 ppm, which is indicative of the nonequivalence of the three phosphorus centers of the molecule. This spectrum is in accordance with a disposition of ligands as shown in Scheme 3, as was confirmed by X-ray diffraction. Also its ^{19}F NMR spectrum corroborates this disposition, clearly showing three types of C_6F_5 groups in the molecule (1:1:1). Regarding its ^1H NMR spectrum, it shows, in addition to the resonances corresponding to the aromatic protons, two doublets centered at 4.94 and 4.88 ppm with relative intensities 1:2, again indicating the presence of two types of hydrogen atoms.

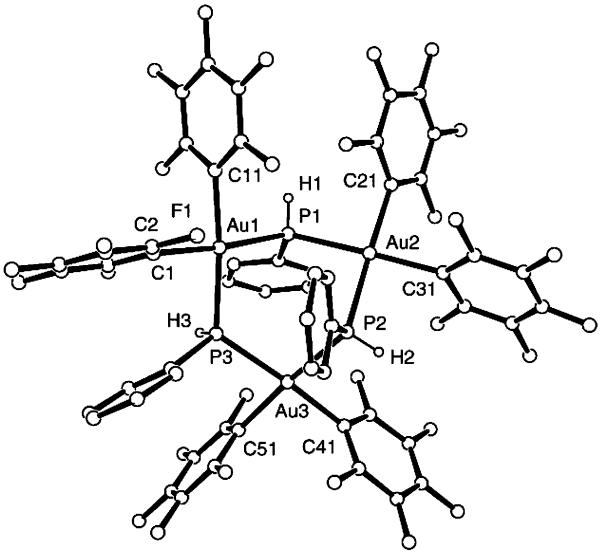


Figure 3. Molecular structure of complex **13**. Hydrogen atoms, except the nonaromatic protons of $PPhH^-$, have been omitted for clarity. Radii are arbitrary.

Finally, by slow diffusion of hexane into a solution of **13** in chloroform, single crystals suitable for its characterization by X-ray diffraction were obtained. This complex crystallizes in the monoclinic system with disordered solvent. It consists (Figure 3) of a hexanuclear ring of alternating square-planar gold(III) and tetrahedral phosphorus atoms in a twisted boat (Figure 4) instead of a chair conformation as shown in [Au(CH$_3$)$_2$(NH$_2$)]$_3$[36] or a planar triangular disposition of gold(I) and phosphorus atoms as in [Au(PIs$_2$)]$_3$.[37] One of the phosphorus atoms (P3) is disordered over two different positions (80:20), so its bond lengths and angles will refer to that with higher occupancy. The Au$-$C bond lengths lie in the range 2.052(8)$-$2.078(7) Å and com-

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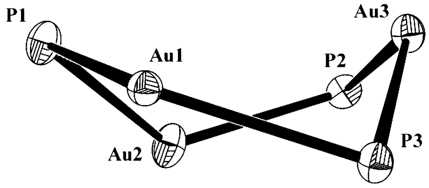

Figure 4. Twisted boat conformation of the six-membered Au−P ring in **13**.

pare well with those found in other gold(III) phosphides,[30] while the Au−P bond lengths (average 2.359 Å) are shorter than in the noncyclic dinuclear complex NBu$_4$[{Au(C$_6$F$_5$)$_3$}$_2$(μ-PPh$_2$)] (average 2.393 Å),[30b] but similar to those found in other cyclic or noncyclic gold(III) phosphides.[30] It is worth noting that in the crystal structure of **13** the distortion of the square-planar environment of the gold centers caused by the formation of the ring produces the opening of the P−Au−P angles (average 94.5°), while in other cyclic phosphides[30,34] or in the amido derivative [Au(CH$_3$)$_2$(NH$_2$)]$_3$[36] the distortion goes in the opposite direction, showing P−Au−P or N−Au−N angles more acute than expected. Probably, the formation of the ring is also responsible for the deviation observed in the Au−P−Au angles, which range from 121.6(1)° to 123.4(1)°.

As the trinuclear cyclic complex that we have just described still presents hydrogen atoms bonded to phosphorus, we treated it with an equimolecular amount of [Au(acac)(PPh$_3$)], leading to the tetranuclear derivative [{Au(C$_6$F$_5$)$_2$(μ-PPhH)}$_2${Au(C$_6$F$_5$)$_2$(μ_3-PPh)Au(PPh$_3$)}] (**14**), which contains two phenylphosphide and one phenylphosphodiide unit. This new complex is obtained as a white solid, soluble in most common organic solvents and insoluble in hexane.

It is worth noting that although **14** can have numerous isomers, its ^{31}P{^{1}H} NMR spectrum shows only the nonequivalence of the four phosphorus atoms of the molecule, displaying two singlets and two doublets with similar intensities and located at −23.6, −12.0, 10.5, and 44.4 ppm, the last one corresponding to the phosphorus of the triphenylphosphine and showing a coupling constant of 282 Hz with the phosphorus of the PPh^{2-} ligand, similar to those observed for other phosphodiides (see Experimental Section).

Regarding its ^{19}F NMR spectrum, it shows a very complicated pattern, although the presence of six triplets in the region corresponding to the *para* fluorine atoms reveals the nonequivalence of the pentafluorophenyl groups.

Experimental Section

Instrumentation. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer using Nujol mulls between polyethylene sheets. C, H, N analyses were carried out with a Perkin-Elmer 240C microanalyzer. Mass spectra were recorded on a HP59987 A Electrospray. ^{31}P{^{1}H}, ^{19}F, and ^{1}H NMR spectra were recorded on a Bruker ARX 300 in CDCl$_3$ solutions. Chemical shifts are quoted relative to H$_3$PO$_4$ (85%) (^{31}P, external), CFCl$_3$ (^{19}F, external), and SiMe$_4$ (^{1}H, external).

General Procedures. Phenylphosphine, Tl(acac), and Ag(OClO$_3$) are commercially available and were purchased from Aldrich and used as received. Other products were prepared by published methods.

Synthesis of [Au(C$_6$F$_5$)(PPhH$_2$)] (1). PPhH$_2$ (0.2 mmol, 0.02 mL) was added to a solution of [Au(C$_6$F$_5$)(tht)][39] (0.2 mmol, 0.090 g) in diethyl ether (20 mL). After stirring for 15 min, the solvent was partially evaporated and cold hexane was added to afford **1** as a white solid. Yield: 0.06 g (65%). ^{31}P{^{1}H}NMR (CDCl$_3$, RT), δ: −46.0 (s, 1P, *P*PhH$_2$). ^{19}F NMR (CDCl$_3$, RT), δ: −116.1 (m, 2F, F$_o$), −157.3 [t, 1F, ^3J(F$_m$−F$_p$) = 20.9 Hz, F$_p$], −161.5 (m, 2F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.82−7.48 (m, 5H, Ph), 6.15 (d, 2H, PPh*H*$_2$). Anal. Calcd for C$_{12}$H$_7$AuF$_5$P (474.13): C, 30.4; H, 1.45. Found: C, 32.2; H, 1.75. Λ_M: 31 Ω^{-1}cm^2 mol^{-1}. ES(−) *m/z* (%): 473 (100).

Synthesis of [Au(C$_6$F$_5$)$_3$(PPhH$_2$)] (2). To a diethyl ether solution (20 mL) of [Au(C$_6$F$_5$)$_3$(tht)][32] (0.2 mmol, 0.157 g) was added PPhH$_2$ (0.2 mmol, 0.02 mL). After 15 min of stirring the solution was concentrated to ca. 5 mL, and by addition of hexane (20 mL) complex **2** was precipitated as a white solid. Yield: 0.13 g (79%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: −59.3 (s, 1P, *P*PhH$_2$). ^{19}F NMR (CDCl$_3$, RT), δ: −120.8 (m, 4F, F$_o$), −155.0 [t, 2F, ^3J(F$_m$−F$_p$) = 19.9 Hz, F$_p$], −160.0 (m, 4F, F$_m$), −122.0 (m, 2F, F$_o$), −156.4 [t, 1F, ^3J(F$_m$−F$_p$) = 20.0 Hz, F$_p$], −161.1 (m, 2F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.63−7.40 (m, 5H, Ph), 5.92 (d, 2H, PPh*H*$_2$). Anal. Calcd for C$_{24}$H$_7$AuF$_{15}$P (808.21): C, 35.65; H, 0.85. Found: C, 36.0; H, 1.1. Λ_M: 14 Ω^{-1} cm^2 mol^{-1}. ES(−) *m/z* (%): 807 (100).

Synthesis of [Au(C$_6$F$_5$)$_3$(μ-PPhH)Au(PPh$_3$)] (3). [Au(acac)(PPh$_3$)][40] (0.2 mmol, 0.112 g) was added to a freshly prepared solution of **2** (0.2 mmol, 0.161 g) in dichloromethane (20 mL). After 1 h stirring, the solvent was partially evaporated and hexane was added to afford **3** as a white solid. Yield: 0.15 g (61%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: 45.1 [d, 1P, ^2J(P−P) = 301 Hz, *P*Ph$_3$], −31.6 (d, 1P, *P*PhH$^-$). ^{19}F NMR (CDCl$_3$, RT), δ: −119.7 (m, 2F, F$_o$), −158.4 [t, 1F, ^3J(F$_m$−F$_p$) = 20.0 Hz, F$_p$], −161.8 (m, 2F, F$_m$), −120.4 (m, 2F, F$_o$), −158.4 [t, 1F, ^3J (F$_m$−F$_p$) = 20.0 Hz, F$_p$], −161.8 (m, 2F, F$_m$), −121.3 (m, 2F, F$_o$), −158.8 [t, 1F, ^3J(F$_m$−F$_p$) = 19.9 Hz, F$_p$], −162.1 (m, 2F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.65−7.18 (m, 20H, Ph), 5.79 (d, 1H, PPh*H*$^-$). Anal. Calcd for C$_{42}$H$_{21}$Au$_2$F$_{15}$P$_2$ (1266.47): C, 39.85; H, 1.65. Found: C, 40.1; H, 2.0. Λ_M: 17 Ω^{-1} cm^2 mol^{-1}.

Synthesis of [Au(C$_6$F$_5$)$_3$(μ-PPhH)Au(PMe$_3$)] (4). To a freshly prepared solution of **2** (0.2 mmol, 0.161 g) in dichloromethane (20 mL) were added [AuCl(PMe$_3$)][41] (0.2 mmol, 0.061 g) and Tl(acac) (0.2 mmol, 0.061 g), and after stirring for 1 h the TlCl formed was filtered off. Partial evaporation of the solvent and addition of hexane led to the precipitation of **4** as a white solid. Yield: 0.15 g (71%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: −8.3 [d, 1P, ^2J(P−P) = 319 Hz, *P*Me$_3$], −32.7 (d, 1P, *P*PhH$^-$). ^{19}F NMR (CDCl$_3$, RT), δ: −120.0 (m, 2F, F$_o$), −158.6 [t, 1F, ^3J(F$_m$−F$_p$) = 20.0 Hz, F$_p$], −162.1 (m, 2F, F$_m$), −120.3 (m, 2F, F$_o$), −158.6 (t, 1F, ^3J(F$_m$,−F$_p$) = 20.0 Hz, F$_p$], −162.1 (m, 2F, F$_m$), −121.3 (m, 2F, F$_o$), −158.8 [t, 1F, ^3J(F$_m$−F$_p$) = 20.0 Hz, F$_p$], −162.1 (m, 2F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.80−7.08 (m, 5H, Ph), 5.65 (d, 1H, PPh*H*$^-$), 1.65 (d, 9H, C*H*$_3$). Anal. Calcd for C$_{27}$H$_{15}$Au$_2$F$_{15}$P$_2$ (1079.96): C, 30.0; H, 1.4. Found: C, 30.1; H, 1.3. Λ_M: 10 Ω^{-1} cm^2 mol^{-1}.

Synthesis of PPN[{Au(C$_6$F$_5$)$_3$}$_2$(μ-PPhH)] (5). To a freshly prepared solution of **2** (0.2 mmol, 0.161 g) in dichloromethane (20 mL) were added [Au(C$_6$F$_5$)$_3$(tht)] (0.2 mmol, 0.157 g) and PPN(acac)[42] (0.2 mmol, 0.127 g). After stirring for 1 h, partial evaporation of the solvent and addition of hexane led to the precipitation of **5** as a white solid. Yield: 0.31 g (76%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: 21.1 (s, 2P, PPN); −46.4 (s, 1P,

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*P*PhH$^-$). ^{19}F NMR (CDCl$_3$, RT), δ: −120.4 (m, 8F, F$_o$), −158.8 [t, 4F, ^3J(F$_m$−F$_p$) = 19.9 Hz, F$_p$], −162.3 (m, 8F, F$_m$), −120.9 (m, 4F, F$_o$), −159.1 [t, 2F, ^3J (F$_m$−F$_p$) = 20.1 Hz, F$_p$], −162.4 (m, 4F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.63−6.79 (m, 35H, Ph), 5.32 (d, 1H, PPh*H*$^-$). Anal. Calcd for $C_{78}H_{36}Au_2F_{30}P_3N$ (2043.91): C, 45.85; H, 1.75; N, 0.7. Found: C, 45.85; H, 2.05; N, 0.75. Λ_M: 82 Ω^{-1} cm^2 mol^{-1}. ES(−) *m*/*z* (%): 1505 [M]$^-$ (100).

Synthesis of PPN[{Au(C$_6$F$_5$)$_3$(μ-PPhH)}$_2$Au] (6). PPN-[Au(acac)$_2$][42] (0.1 mmol, 0.093 g) was added to a solution of compound **2** (0.2 mmol, 0.161 g) in dichloromethane (20 mL). After 1 h of stirring the solvent was evaporated, and addition of hexane led to the precipitation of **6** as a white solid. Yield: 0.14 g (58%). (NMR signals corresponding to two different diastereoisomeric pairs.) ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: 21.1 (s, 2P, PPN), −31.0 (s, 2P, *P*PhH$^-$), −33.3 (s, 2P, *P*PhH$^-$). ^{19}F NMR (CDCl$_3$, RT), δ: −119.7 (m, 4F, F$_o$), −159.3 [t, 2F, ^3J(F$_m$−F$_p$) = 19.2 Hz, F$_p$], −162.5 (m, 4F, F$_m$), −120.6 (m, 2F, F$_o$), −159.7 [t, 1F, ^3J(F$_m$−F$_p$) = 20.0 Hz, F$_p$], −162.5 (m, 2F, F$_m$); −120.0 (m, 4F, F$_o$), −159.4 [t 2F, ^3J(F$_m$−F$_p$) = 19.2 Hz, F$_p$], −162.5 (m, 4F, F$_m$), −120.6 (m, 2F, F$_o$), −159.7 [t, 1F, ^3J(F$_m$−F$_p$) = 20.0 Hz, F$_p$], −162.5 (m, 2F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.75−7.12 (m, 40H, Ph), 5.70 (d, 2H, PPh*H*$^-$), 5.53 (d, 2H, PPh*H*$^-$). Anal. Calcd for $C_{84}H_{42}Au_3F_{30}P_4N$ (2350.06): C, 42.95; H, 1.8; N, 0.6; Found: C, 42.8; H, 1.9; N, 0.6. Λ_M: 94 Ω^{-1} cm^2 mol^{-1}. ES(−) *m*/*z* (%): 1811 [M]$^-$ (100).

Synthesis of PPN[{Au(C$_6$F$_5$)$_3$(μ-PPhH)}$_2$Ag] (7). A solution of Ag(OClO$_3$) (0.1 mmol, 0.021 g) in diethyl ether (10 mL) was added to a solution of compound **2** (0.2 mmol, 0.161 g) and PPN(acac) (0.2 mmol, 0.127 g) 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 **7** as a white solid. Yield: 0.11 g (48%). (NMR signals corresponding to two different diastereoisomeric pairs.) ^{31}P{^{1}H} NMR (CDCl$_3$, 223 K), δ: 21.1 (s, 2P, PPN), −66.3 [s, 2P, *J*(P−^{109}Ag) = 514, *J*(P−^{107}Ag) = 445 Hz, *P*PhH$^-$]; −69.3 [s, 2P, *J*(P−^{109}Ag) = 511, *J*(P−^{107}Ag) = 444 Hz, *P*PhH$^-$]. ^{19}F NMR (CDCl$_3$, RT), δ: −119.7 (m, 4F, F$_o$), −158.8 [t, 2F, ^3J(F$_m$−F$_p$) = 20.3 Hz, F$_p$], −161.9 (m, 4F, F$_m$), −120.8 (m, 2F, F$_o$), −159.2 [t, 1F, ^3J (F$_m$−F$_p$) = 20.0 Hz, F$_p$], −161.9 (m, 2F, F$_m$); −120.2 (m, 4F, F$_o$), −159.0 [t, 2F, ^3J(F$_m$−F$_p$) = 20.3 Hz, F$_p$], −161.9 (m, 4F, F$_m$), −120.8 (m, 2F, F$_o$), −159.3 [t, 1F, ^3J (F$_m$−F$_p$) = 20.0 Hz, F$_p$], −161.9 (m, 2F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.69−7.12 (m, 40H, Ph), 4.80 (d, 2H, PPh*H*$^-$); 4.66 (d, 2H, PPh*H*$^-$). Anal. Calcd for $C_{84}H_{42}AgAu_2F_{30}P_4N$ (2260.87): C, 44.65; H, 1.85; N, 0.6. Found: C, 45.05; H, 2.0; N, 0.6. Λ_M: 97 Ω^{-1} cm^2 mol^{-1}. ES(−) *m*/*z* (%): 1723 [M]$^-$ (100).

Synthesis of [Au(C$_6$F$_5$)$_3$(μ_3-PPh){Au(PPh$_3$)}$_2$] (8). Method 1. [Au(acac)(PPh$_3$)] (0.2 mmol, 0.112 g) was added to a freshly prepared solution of **2** (0.1 mmol, 0.081 g) in dichloromethane (20 mL). After 1 h stirring, the solvent was partially evaporated and hexane was added to afford **8** as a white solid. Yield: 0.13 g (74%).

Method 2. [Au(acac)(PPh$_3$)] (0.1 mmol, 0.056 g) was added to a solution of compound **3** (0.1 mmol, 0.127 g) in dichloromethane (20 mL). After 1 h of stirring the solvent was evaporated, and addition of hexane led to the precipitation of **8** as a white solid. Yield: 0.12 g (68%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: 45.1 [d, 2P, ^2J(P−P) = 268 Hz, *P*Ph$_3$), 1.1 (t, 1P, *P*Ph^{2-}). ^{19}F NMR (CDCl$_3$, RT), δ: −117.5 (m, 4F, F$_o$), −160.5 [t, 2F, ^3J(F$_m$−F$_p$) = 20.0 Hz, F$_p$], −162.7 (m, 4F, F$_m$), −120.7 (m, 2F, F$_o$), −160.3 [t, 1F, ^3J (F$_m$−F$_p$) = 20.1 Hz, F$_p$], −162.6 (m, 2F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.55−6.92 (m, 35H, Ph). Anal. Calcd for $C_{60}H_{35}Au_3F_{15}P_3$ (1724.72): C, 41.75; H, 2.05. Found: C, 41.85; H, 2.5. Λ_M: 12 Ω^{-1} cm^2 mol^{-1}.

Synthesis of PPN[Au(C$_6$F$_5$)$_3$(μ_3-PPh){Au(C$_6$F$_5$)}{Au(PPh$_3$)}] (9). To a solution of compound **3** (0.1 mmol, 0.127 g) in dichloromethane (20 mL) were added [Au(C$_6$F$_5$)(tht)] (0.1 mmol, 0.045 g) and PPN(acac) (0.1 mmol, 0.064 g). After 1 h of stirring the solvent was evaporated and addition of hexane led to the precipitation of **9** as a white solid. Yield: 0.13 g (62%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: 45.0 [d, 1P, ^2J(P−P) = 254 Hz, *P*Ph$_3$), 7.0 (t, 1P, *P*Ph^{2-}). ^{19}F NMR (CDCl$_3$, RT), δ: −114.9 (m, 2F, F$_o$), −161.4 [t, 1F, ^3J(F$_m$−F$_p$) = 19.8 Hz, F$_p$], −163.3 (m, 2F, F$_m$), −116.3 (m, 2F, F$_o$), −161.4 [t, 1F, ^3J(F$_m$−F$_p$) = 20.4 Hz, F$_p$], −163.7 (m, 2F, F$_m$), −117.1 (m, 2F, F$_o$), −162.7 [t, 1F, ^3J(F$_m$−F$_p$) = 20.4 Hz, F$_p$], −163.7 (m, 2F, F$_m$), −118.8 (m, 2F, F$_o$), −162.7 [t, 1F, ^3J(F$_m$−F$_p$) = 20.4 Hz, F$_p$], −164.5 (m, 2F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.80−6.76 (m, 50H, Ph). Anal. Calcd for $C_{84}H_{50}Au_3F_{20}P_4N$ (2167.78): C, 46.55; H, 1.85; N, 0.55. Found: C, 49.0; H, 1.9; N, 0.9. Λ_M: 100 Ω^{-1} cm^2 mol^{-1}. ES(−) *m*/*z* (%): 1629 [M]$^-$ (95).

Synthesis of PPN[{Au(C$_6$F$_5$)$_3$}$_2$(μ_3-PPh){Au(PPh$_3$)}] (10). [Au(acac)(PPh$_3$)] (0.1 mmol, 0.056 g) was added to a freshly prepared solution of **5** (0.1 mmol, 0.204 g) in dichloromethane (20 mL). After 1 h of stirring, the solvent was partially evaporated and hexane was added to afford **10** as a white solid. Yield: 0.05 g (20%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: 21.1 (s, 2P, PPN), 42.6 (d, 1P, ^2J(P−P) = 269 Hz, *P*Ph$_3$], −8.7 (d, 1P, *P*Ph^{2-}). ^{19}F NMR (CDCl$_3$, RT), δ: −116.6 (m, 4F, F$_o$), −160.8 [t, 2F, ^3J(F$_m$−F$_p$) = 20.2 Hz, F$_p$], −162.9 (m, 2F, F$_m$), −117.8 (m, 4F, F$_o$), −161.1 [t, 1F, ^3J(F$_m$−F$_p$) = 20.3 Hz, F$_p$], −162.9 (m, 4F, F$_m$), −119.9 (m, 4F, F$_o$), −161.1 [t, 2F, ^3J(F$_m$−F$_p$) = 20.3 Hz, F$_p$], −163.8 (m, 4F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.63−6.65 (m, 50H, Ph). Anal. Calcd for $C_{96}H_{50}Au_3F_{30}P_4N$ (2502.57): C, 46.1; H, 2.0; N, 0.55. Found: C, 45.7; H, 2.45; N, 0.5. Λ_M: 108 Ω^{-1} cm^2 mol^{-1}.

Synthesis of (PPN)$_2$[{Au(C$_6$F$_5$)$_3$}$_2$(μ_3-PPh){Au(C$_6$F$_5$)}] (11). To a freshly prepared solution of **5** (0.1 mmol, 0.204 g) in dichloromethane (20 mL) were added [Au(C$_6$F$_5$)(tht)] (0.1 mmol, 0.045 g) and PPN(acac) (0.1 mmol, 0.064 g). After stirring for 1 h partial evaporation of the solvent and addition of hexane led to the precipitation of **11** as a white solid. Yield: 0.18 g (61%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: 21.1 (s, 4P, PPN), −1.4 (s, 1P, *P*Ph^{2-}). ^{19}F NMR (CDCl$_3$, RT), δ: −115.2 (m, 2F, F$_o$), −161.9 [t, 1F, ^3J(F$_m$−F$_p$) = 19.8 Hz, F$_p$], −164.5 (m, 2F, F$_m$), −116.6 (m, 4F, F$_o$), −163.4 [t, 2F, ^3J(F$_m$−F$_p$) = 20.4 Hz, F$_p$], −164.5 (m, 4F, F$_m$), −117.9 (m, 4F, F$_o$), −163.4 [t, 2F, ^3J(F$_m$−F$_p$) = 20.4 Hz, F$_p$], −164.5 (m, 4F, F$_m$), −118.8 (m, 4F, F$_o$), −163.4 [t, 2F, ^3J(F$_m$−F$_p$) = 20.4 Hz, F$_p$], −164.5 (m, 4F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.64−7.33 (m, 65H, Ph). Anal. Calcd for $C_{120}H_{65}Au_3F_{35}P_5N_2$ (2945.62): C, 48.95; H, 2.2; N, 0.95. Found: C, 48.95; H, 2.0; N, 0.8. Λ_M: 191 Ω^{-1} cm^2 mol^{-1}. ES(−) *m*/*z* (%): 934 [M]$^{2-}$ (25).

Synthesis of (PPN)$_3$[{(Au(C$_6$F$_5$)$_3$)$_2$(μ_3-PPh)$_2$}$_2$Au] (12). To a freshly prepared solution of **5** (0.2 mmol, 0.409 g) in dichloromethane (20 mL) was added PPN[Au(acac)$_2$] (0.1 mmol, 0.093 g). After stirring for 1 h, partial evaporation of the solvent and addition of hexane led to the precipitation of **12** as a white solid. Yield: 0.37 g (76%). ^{31}P{^{1}H} NMR (CDCl$_3$, RT), δ: 21.1 (s, 6P, PPN), 12.8 (s, 2P, *P*Ph^{2-}). ^{19}F NMR (CDCl$_3$, RT), δ: −116.8 (m, 4F, F$_o$), −158.8 [t, 2F, ^3J(F$_m$−F$_p$) = 19.9 Hz, F$_p$], −162.1 (m, 4F, F$_m$), −117.4 (m, 4F, F$_o$), −158.8 [t 2F, ^3J(F$_m$−F$_p$ = 19.9 Hz, F$_p$], −162.4 (m, 4F, F$_m$), −118.9 (m, 4F, F$_o$), −158.8 [t, 2F, ^3J(F$_m$−F$_p$) = 19.9 Hz, F$_p$], −162.4 (m, 4F, F$_m$), −120.0 (m, 8F, F$_o$), −162.6 [t, 4F, ^3J(F$_m$−F$_p$) = 20.3 Hz, F$_p$], −164.3 (m, 8F, F$_m$), −120.3 (m, 4F, F$_o$), −161.7 [t, 2F, ^3J(F$_m$−F$_p$) = 20.3 Hz, F$_p$], −163.4 (m, 4F, F$_m$). ^{1}H NMR (CDCl$_3$, RT), δ: 7.68−6.57 (m, 100H, Ph). Anal. Calcd for $C_{192}H_{100}$-$Au_5F_{60}P_8N_3$ 4821.36): C, 47.85; H, 2.1; N, 0.9. Found: C, 47.4; H, 2.45; N, 0.9. Λ_M: 284 Ω^{-1} cm^2 mol^{-1}.

Synthesis of [Au(C$_6$F$_5$)$_2$(μ-PPhH)]$_3$ (13). PPhH$_2$ (0.4 mmol, 0.045 mL) was added to a solution of [Au(C$_6$F$_5$)$_2$(μ-Cl)$_2$][43] (0.2 mmol, 0.227 g) in diethyl ether (20 mL), leading to a yellow solution. After stirring for 90 min, the solvent was partially evaporated and hexane was added to afford **13** as a

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pale yellow solid. Yield: 0.212 g (83%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, RT), δ: −12.0 (s, 1P, *P*PhH⁻), −22.0 (s, 2P, *P*PhH⁻). ^{19}F NMR ($CDCl_3$, RT), δ: −121.6 (m, 4F, F_o), −154.5 [t, 2F, $^3J(F_m-F_p) =$ 20.0 Hz, F_p], −159.5 (m, 4F, F_m), −121.0 (m, 8F, F_o), −153.9 [t, 2F, $^3J(F_m-F_p$ = 19.8 Hz, F_p], −154.2 [t, 2F, $^3J(F_m-F_p$ = 19.8 Hz, F_p], −159.1 (m, 8F, F_m). ^1H NMR ($CDCl_3$, RT), δ: 7.70−6.90 (m, 15H, Ph), 4.94 [dm, 1H, *J*(P−H) = 397 Hz, PPh*H*⁻], 4.88 [dm, 2H, *J*(P−H) = 385 Hz, PPh*H*⁻]. Anal. Calcd for $C_{54}H_{18}Au_3F_{30}P_3$ (1920.56): C, 35.05; H, 1.35. Found: C, 33.8; H, 0.95. Λ_M: 28 Ω^{-1} cm^2 mol^{-1}.

Synthesis of [{Au(C_6F_5)$_2$(*μ*-PPhH)}$_2${Au(C_6F_5)$_2$(*μ*$_3$-PPh)(AuPPh$_3$)}] (14). To a solution of **13** (0.2 mmol, 0.384 g) in dichloromethane (20 mL) was added [Au(acac)PPh_3] (0.2 mmol, 0.112 g). After 1 h stirring, the solvent was partially evaporated and hexane was added to afford **14** as a white solid. Yield: 0.252 g (53%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, RT), δ: 44.4 [d, 1P, $^2J(P-P)$ = 282 Hz, *P*Ph$_3$], −10.5 (d, 1P, *P*Ph^{2-}), −12.0 (s, 1P, *P*PhH⁻), −23.6 (s, 1P, *P*PhH⁻). ^{19}F NMR ($CDCl_3$, RT), δ: −118.2 (m, 1F, F_o), −118.8 (m, 1F, F_o), −119.2 (m, 1F, F_o), −120.6 (m, 2F, F_o), −121.5 (m, 3F, F_o), −121.7 (m, 1F, F_o), −122.6 (m, 1F, F_o), −123.1 (m, 1F, F_o), −123.5 (m, 4F, F_o), −155.6 [t, 1F, $^3J(F_m-F_p)$ = 19.4 Hz, F_p], −155.6 [t, 1F, $^3J(F_m-F_p)$ = 18.9 Hz, F_p], −155.8 [t, 1F, $^3J(F_m-F_p)$ = 19.8 Hz, F_p], −156.3 [t, 1F, $^3J(F_m-F_p)$ = 19.0 Hz, F_p], −156.4 [t, 1F, $^3J(F_m-F_p)$ = 19.0 Hz, F_p], −157.9 [t, 1F, $^3J(F_m-F_p)$ = 20.0 Hz, F_p], −159.3 (m, 3F, F_m), −159.7 (m, 3F, F_m), −160.3 (m, 2F, F_m), −160.7 (m, 2F, F_m), −161.1 (m, 2F, F_m). Anal. Calcd for $C_{72}H_{32}Au_4F_{30}P_4$ (2378,71): C, 35.85; H, 1.2. Found: C, 36.35; H, 1.35. Λ_M: 54 Ω^{-1} cm^2 mol^{-1}.

Crystallography. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Bruker Smart 1000 CCD (**5**, **8**) or Nonius Kappa CCD diffractometer (**13**) equipped with an Oxford Instruments low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ = 0.71073 Å). Scan type: ω and ϕ. Absorption corrections: numerical (based on multiple scans). The structures were solved by direct methods or the heavy-atom method and refined on F^2 using the program SHELXL-97.[44] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model, except for the PH hydrogen of compound **5**, which was refined freely. Further details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are collected in Tables 1−4 and crystal structures of complexes **5**, **8**, and **13** in Figures 1−4. CCDC-243270−243272 contain supplementary crystallographic data for this paper. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for Complex 13

Au(1)−C(11)	2.066(7)	Au(1)−C(1)	2.075(6)
Au(1)−P(1)	2.357(2)	Au(1)−P(3)	2.371(2)
Au(2)−C(31)	2.063(7)	Au(2)−C(21)	2.078(7)
Au(2)−P(1)	2.350(2)	Au(2)−P(2)	2.352(2)
Au(3)−C(41)	2.052(8)	Au(3)−C(51)	2.066(7)
Au(3)−P(2)	2.351(2)	Au(3)−P(3)	2.371(2)
C(11)−Au(1)−C(1)	87.9(2)	C(11)−Au(1)−P(1)	87.33(16)
C(1)−Au(1)−P(1)	174.53(18)	C(11)−Au(1)−P(3)	171.80(18)
C(1)−Au(1)−P(3)	91.00(18)	P(1)−Au(1)−P(3)	93.32(7)
C(31)−Au(2)−C(21)	90.3(3)	C(31)−Au(2)−P(1)	174.85(19)
C(21)−Au(2)−P(1)	89.42(19)	C(31)−Au(2)−P(2)	87.81(19)
C(21)−Au(2)−P(2)	176.0(2)	P(1)−Au(2)−P(2)	92.74(6)
C(41)−Au(3)−C(51)	89.9(3)	C(41)−Au(3)−P(2)	87.8(2)
C(51)−Au(3)−P(2)	174.39(19)	C(41)−Au(3)−P(3)	174.5(2)
C(51)−Au(3)−P(3)	85.09(18)	P(2)−Au(3)−P(3)	97.40(7)
C(61)−P(1)−Au(2)	106.8(2)	C(61)−P(1)−Au(1)	112.4(2)
Au(2)−P(1)−Au(1)	121.59(8)	C(71)−P(2)−Au(3)	109.1(2)
C(71)−P(2)−Au(2)	108.8(2)	Au(3)−P(2)−Au(2)	123.18(10)
C(81)−P(3)−Au(3)	110.8(2)	C(81)−P(3)−Au(1)	112.1(2)
Au(3)−P(3)−Au(1)	123.39(9)		

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Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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