Ability of a Au(III)−N Unit to Bond Two Aurophilically Interacting Gold(I) Centers[†]

Eduardo J. Fernández, Manuel Gil, and M. Elena Olmos

Departamento de Química, Universidad de La Rioja, Grupo de Síntesis Química de La Rioja,
UA-CSIC, Madre de Dios 51, E-26006 Logroño, Spain

Olga Crespo and Antonio Laguna*

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

Peter G. Jones

Institüt für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329,
D-38023 Braunschweig, Germany

Received January 23, 2001

The monohapto neutral 2-(diphenylphosphino)aniline (PNH_2) complexes $[Au(C_6F_5)_2X(PNH_2)]$ (X = C_6F_5 (**1**), Cl (**2**)) have been obtained from $[Au(C_6F_5)_3(tht)]$ or $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$ and PNH_2, and the cationic $[Au(C_6F_5)_2(PNH_2)]ClO_4$ (**3**) has been similarly prepared from $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ and PNH_2 or from **2** and $AgClO_4$. The neutral amido complex $[Au(C_6F_5)_2(PNH)]$ (**4**) can be obtained by deprotonation of **3** with PPN(acac) (acac = acetylacetonate) or by treatment of the chloro complex **2** with Tl(acac). It reacts with $[Ag(OClO_3)(PPh_3)]$ or $[Au(OClO_3)(PPh_3)]$ to give the dinuclear species $[Au(C_6F_5)_2\{PNH(MPPh_3)\}]ClO_4$ (M = Ag (**5**), Au (**6**)). The latter can also be obtained by reaction of equimolar amounts of **3** and $[Au(acac)(PPh_3)]$; when the molar ratio of the same reagents is 1:2, the trinuclear cationic complex $[Au(C_6F_5)_2\{PN(AuPPh_3)_2\}]ClO_4$ (**7**) is obtained. The crystal structures of complexes **2**−**4** and **7** have been established by X-ray crystallography; the last-mentioned displays an unusual Au(I)−Au(III) interaction.

Introduction

Polyfunctional ligands with P-, S-, or N-donor centers are often instrumental in the preparation of a variety of polynuclear complexes. In the case of gold, these complexes may be used for a number of applications, including chemotherapy, diagnostics, electron microscopy, catalysis, and surface technology.[1−5] One such ligand is the P,N-donor 2-(diphenylphosphino)aniline (PNH_2), which has been employed for the synthesis of a number of derivatives of W, Ni, Pd, Pt, Rh, Os, and Re in which it usually acts as bidentate chelating ligand and the nitrogen center is sometimes deprotonated.[6−11] In contrast, only a few group 11 metal complexes of PNH_2 have been reported[12] and the only oxidation state represented is +1, with the exception of the Cu(II) derivative $[Cu(PNH_2)_2](BF_4)_2$.[12d]

There is a general acceptance of the relativistic effects exhibited by the elements of the third transition series.[13] These effects reach a maximum at gold, and the topic has recently been reviewed in terms of theoretical and experimental evidence,[14] although the theoretical understanding of such interactions still remains in a preliminary state.[15] A strong attractive and energetically favorable interaction has been observed between gold(I) atoms (d^{10} configuration) in numerous polynuclear gold compounds,[16−21] while gold(I)−gold(III) interac-

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[†] Dedicated to Prof. R. Usón on the occasion of his 75th birthday.

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10.1021/ic0100875 CCC: $20.00

tions have only been previously described in mixed-valence doubly bridged ylide systems where the gold centers are forced to be in close proximity,[22−25] in the polynuclear sulfur-centered complex $[\{S(Au^I{}_2dppf)\}_2\{Au^{III}(C_6F_5)\}]OTf$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene),[26] and in the derivative $[Au^IAu^{III}Me_2(PMe_3)_2(C_4F_6)]$.[27] It is notable that, apart from these, not too many interactions have been observed in other d^8-d^{10} systems.[28]

Taking these facts into account, we have centered our interest on the study of gold(III) derivatives of 2-(diphenylphosphino)aniline and their reactivity toward Au(I) or Ag(I) species in order to establish whether they display unusual new metal−metal interactions.

Experimental Section

Reagents. $AgClO_4$ was purchased from Aldrich and used as received. The compounds PNH_2,[29] $[Au(C_6F_5)_3(tht)]$,[30] $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$,[31] $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$,[32] $[Au(C_6F_5)_2(acac)]$,[31] Tl(acac),[33] PPN(acac),[34] $[Ag(OClO_3)(PPh_3)]$,[35] and $[Au(acac)(PPh_3)]$[36] were prepared by literature methods.

Caution! Perchlorate salts with organic cations may be explosive.

Apparatus. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer and on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} M acetone solutions with a Jenway 4010 conductimeter. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. Mass spectra were recorded on a VG Autospec using FAB techniques and nitrobenzyl alcohol as matrix and on a HP59987 A Electrospray. ^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, external).

Synthesis of $[Au(C_6F_5)_2X(PNH_2)]$ (X = C_6F_5 (1), Cl (2)). To a dichloromethane solution (20 mL) of $[Au(C_6F_5)_3(tht)]$ (0.2 mmol, 0.16 g) or $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$ (0.1 mmol, 0.11 g) was added PNH_2 (0.2 mmol, 0.06 g). After 30 min of stirring the solution was concentrated to ca. 5 mL and addition of hexane (20 mL) precipitated complexes **1** or **2** as white solids. Yield: 73 (**1**), 85% (**2**). Λ_M: 3 (**1**), 3 (**2**) Ω^{-1} cm^2 mol^{-1}. FAB/MS: $[M]^+$ at m/z = 975 (3%, **1**). Anal. Calcd for $C_{36}H_{16}AuF_{15}NP$ (**1**): C, 44.35; H, 1.65; N, 1.45. Found: C, 43.8; H, 1.6; N, 1.4. Calcd for $C_{30}H_{16}AuClF_{10}NP$ (**2**): C, 42.7; H, 1.9: N, 1.65. Found: C, 42.85; H, 2.25; N, 1.95. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: (**1**) 12.0 (m); (**2**) 20.7 (m). ^{19}F NMR ($CDCl_3$), δ: (**1**) −119.9 (m, 4F, F_m), −157.1 [t, 2F, $^3J(F_m-F_p)$ = 19.8 Hz, F_p], −161.0 (m, 4F, F_o), −121.9 (m, 2F, F_m), −157.5 [t, 1F, $^3J(F_m-F_p)$ = 19.9 Hz, F_p], −161.3 (m, 2F, F_o); (**2**) −121.6 (m, 2F, F_m), −156.8 [t, 1F, $^3J(F_m-F_p)$ = 19.9 Hz, F_p], −160.4 (m, 2F, F_o), −122.9 (m, 2F, F_m), −156.8 [t, 1F, $^3J(F_m-F_p)$ = 19.9 Hz, F_p], −161.1 (m, 2F, F_o). ^1H NMR ($CDCl_3$), δ: (**1**) 7.58−6.64 (m, 14H, aromatic protons), 3.8 (m, 2H, NH_2); (**2**) 7.72−6.67 (m, 14H, aromatic protons), 3.9 (m, 2H, NH_2).

Synthesis of $[Au(C_6F_5)_2(PNH_2)]ClO_4$ (3). This complex was obtained by two methods.

Method a. To a freshly prepared solution of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ (0.2 mmol) was added PNH_2 (0.2 mmol, 0.06 g), whereupon a white solid started to form. The mixture was stirred for 2 h to complete the precipitation of **3,** which was filtered off and washed with diethyl ether. Yield: 90%.

Method b. To an acetone solution of **2** (0.2 mmol, 0.17 g) was added $AgClO_4$ (0.2 mmol, 0.04 g). After stirring of the solution for 2 h, the AgCl formed was filtered off, the resulting solution concentrated in vacuo, and 20 mL of diethyl ether was added to precipitate **3** as a white solid. Yield: 85%. Λ_M: 78 Ω^{-1} cm^2 mol^{-1}. FAB/MS: $[M]^+$ at m/z = 808 (87%). Anal. Calcd for $C_{30}H_{16}AuClF_{10}NO_4P$: C, 39.7; H, 1.8; N, 1.55. Found: C, 40.15; H, 1.45; N, 1.45. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 45.1 (m). ^{19}F NMR ($CDCl_3$), δ: −121.3 (m, 2F, F_m), −154.1 [t, 1F, $^3J(F_m-F_p)$ = 19.9 Hz, F_p], −159.8 (m, 2F, F_o), −122.0 (m, 2F, F_m), −154.6 [t, 1F, $^3J(F_m-F_p)$ = 20.1 Hz, F_p], −160.0 (m, 2F, F_o). ^1H NMR ($CDCl_3$), δ: 8.03−7.51 (m, 14H, aromatic protons).

Synthesis of $[Au(C_6F_5)_2(PNH)]$ (4). This complex was obtained by three methods.

Method a. To a solution of $[Au(C_6F_5)_2(acac)]$ (0.2 mmol, 0.13 g) in 20 mL of dichloromethane under a nitrogen atmosphere was added PNH_2 (0.2 mmol, 0.06 g); the solution immediately turned yellow. After 30 min of stirring it was concentrated to ca. 5 mL and hexane (20 mL) was added to precipitate **4** as a yellow solid. Yield: 36%.

Method b. To a dichloromethane solution of **2** (0.2 mmol, 0.17 g) under a nitrogen atmosphere was added Tl(acac) (0.2 mmol, 0.06 g). The mixture was stirred for 3 h, and the TlCl formed was filtered off over Celite. The resulting yellow solution was concentrated in vacuo, and 20 mL of hexane was added to precipitate **4** as a yellow solid. Yield: 54%.

Method c. To a solution of **3** (0.2 mmol, 0.18 g) in 20 mL of dichloromethane under a nitrogen atmosphere was added PPN(acac) (0.2 mmol, 0.13 g); the solution immediately turned yellow. After being stirred for 30 min, the solution was evaporated and diethyl ether was added to precipitate the $PPNClO_4$ formed, which was filtered off over Celite. The resulting yellow solution was concentrated in vacuo, and 20 mL of hexane was added to precipitate **4** as a yellow solid. Yield: 57%. Λ_M: 2 Ω^{-1} cm^2 mol^{-1}. FAB/MS: $[M]^+$ at m/z = 807 (100%). Anal. Calcd for $C_{30}H_{15}AuF_{10}NP$: C, 44.65; H, 1.85; N, 1.75. Found: C, 45.0; H, 2.0; N, 1.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 39.5 (m). ^{19}F NMR ($CDCl_3$), δ: −121.3 (m, 2F, F_m), −156.8 [t, 1F, $^3J(F_m-F_p)$ = 19.7 Hz, F_p], −161.1 (m, 2F, F_o), −121.5 (m, 2F, F_m), −157.0 [t, 1F, $^3J(F_m-F_p)$ = 19.9 Hz, F_p], −161.7 (m, 2F, F_o). ^1H NMR ($CDCl_3$), δ: 7.60−6.44 (m, 14H, aromatic protons), 5.19 (s, 1H, NH).

Synthesis of $[Au(C_6F_5)_2\{PNH(AgPPh_3)\}]ClO_4$ (5). To a solution of **4** (0.2 mmol, 0.16 g) in dichloromethane under nitrogen atmosphere was added $[Ag(OClO_3)(PPh_3)]$ (0.2 mmol, 0.09 g). After 30 min of stirring the solution was concentrated in vacuo to ca. 5 mL, and addition of diethyl ether (20 mL) precipitated complex **5** as a yellow solid. Yield: 25%. Λ_M: 83 Ω^{-1} cm^2 mol^{-1}. ES/MS: $[M]^+$ at m/z = 1177 (7%). Anal. Calcd for: $C_{48}H_{30}AgAuClF_{10}NO_4P_2$: C, 45.15; H, 2.35; N, 1.1. Found: C, 45.45; H, 2.5; N, 1.05. $^{31}P\{^1H\}$ NMR (HDA, 298 K), δ: 45.2 (m, 1P, PPh_2), 14.1 (dm, 1P, $AgPPh_3$). $^{31}P\{^1H\}$ NMR (HDA, 223 K), δ: 45.6 (m, 1P, PPh_2), 13.0 [dd, 1P, $J(^{109}Ag-P)$ =

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803 Hz, $J(^{107}Ag-P) = 691$ Hz, $AgPPh_3$]. ^{19}F NMR (HDA), δ: −121.0 (m, 2F, F_m), −158.2 [t, 1F, $^3J(F_m-F_p) = 19.9$ Hz, F_p], −162.6 (m, 2F, F_o), −121.7 (m, 2F, F_m), −158.9 [t, 1F, $^3J(F_m-F_p) = 19.9$ Hz, F_p], −162.7 (m, 2F, F_o). ^1H NMR (HDA), δ: 7.79−6.52 (m, 14H, aromatic protons).

Synthesis of [Au(C_6F_5)$_2${PNH(AuPPh$_3$)}]ClO$_4$ (6). This complex was obtained by two methods.

Method a. To a solution of **4** (0.2 mmol, 0.16 g) in THF under nitrogen atmosphere was added a freshly prepared solution of [Au($OClO_3$)PPh_3] (0.2 mmol) (obtained by addition of the equimolecular amount of $AgClO_4$ to a THF solution of [AuCl(PPh_3)] under nitrogen at 0 °C). After 30 min of stirring the solution was concentrated in vacuo to ca. 5 mL, and addition of diethyl ether (20 mL) precipitated complex **6** as an orange solid. Yield: 42%.

Method b. To a solution of **3** (0.2 mmol, 0.18 g) in 20 mL of dichloromethane under a nitrogen atmosphere was added [Au(acac)(PPh_3)] (0.2 mmol, 0.11 g); the solution turned orange. After 30 min of stirring the solution was concentrated to ca. 5 mL, and diethyl ether added to precipitate **6** as an orange solid. Yield: 47%. Λ_M: 86 Ω^{-1} cm^2 mol^{-1}. ES/MS: $[M]^+$ at $m/z = 1266$ (95%). Anal. Calcd for $C_{48}H_{30}Au_2ClF_{10}NO_4P_2$: C, 42.2; H, 2.2; N, 1.05. Found: C, 42.45; H, 2.3; N, 1.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 42.4 (m, 1P, PPh_2), 29.3 (s, 1P, $AuPPh_3$). ^{19}F NMR ($CDCl_3$), δ: −121.3 (m, 2F, F_m), −155.0 [t, 2F, $^3J(F_m-F_p) = 19.7$ Hz, F_p], −159.8 (m, 2F, F_o), −121.6 (m, 2F, F_m), −155.1 [t, 1F, $^3J(F_m-F_p) = 19.7$ Hz, F_p], −160.9 (m, 2F, F_o). ^1H NMR ($CDCl_3$), δ: 8.05−7.07 (m, 14H, aromatic protons).

Synthesis of [Au(C_6F_5)$_2${PN(AuPPh$_3$)$_2$}]ClO$_4$ (7). This complex was obtained by two methods.

Method a. To a solution of **3** (0.1 mmol, 0.09 g) in 20 mL of dichloromethane under a nitrogen atmosphere was added [Au(acac)(PPh_3)] (0.2 mmol, 0.11 g); the solution became yellow. After 30 min of stirring the solution was concentrated in vacuo, and addition of 20 mL of diethyl ether precipitated **7** as a yellow solid. Yield: 50%.

Method b. To a dichloromethane solution of **6** (0.1 mmol, 0.14 g) under a nitrogen atmosphere was added [Au(acac)(PPh_3)] (0.1 mmol, 0.06 g); the solution turned yellow. After 30 min of stirring the solution was concentrated to ca. 5 mL, and diethyl ether was added to precipitate **7** as a yellow solid. Yield: 37%. Λ_M: 79 Ω^{-1} cm^2 mol^{-1}. ES/MS: $[M]^+$ at $m/z = 1725$ (16%). Anal. Calcd for $C_{66}H_{45}Au_3ClF_{10}NO_4P_3$: C, 43.45; H, 2.45; N, 0.8. Found: C, 43.8; H, 2.7; N, 1.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 46.3 (m, 1P, PPh_2), 27.5 (s, 2P, $AuPPh_3$). ^{19}F NMR ($CDCl_3$), δ: −116.2 (m, 2F, F_m), −153.7 [t, 2F, $^3J(F_m-F_p) = 20.4$ Hz, F_p], −159.2 (m, 2F, F_o), −121.8 (m, 2F, F_m), −155.3 [t, 1F, $^3J(F_m-F_p) = 19.9$ Hz, F_p], −160.1(m, 2F, F_o). ^1H NMR ($CDCl_3$), δ: 7.58−7.08 (m, 14H, aromatic protons).

Crystal Structure Determinations. The crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Siemens P4 (**2**), Siemens SMART (**3**), or Bruker SMART (**4**, **7**) diffractometer. Data were collected using monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) in ω-scan mode (**2**, **3**) or with ω- and ϕ-scans (**4**, **7**). Absorption corrections were applied on the basis of ψ-scans for **2**, whereas for **3**, **4,** and **7** the program SADABS, based on multiple scans, was used. The structures were solved by Patterson (**2**, **4**) or direct methods (**3**, **7**) and refined on F^2 using the program SHELXL-97.[37] All non-hydrogen atoms were refined anisotropically, except for solvent carbon. Aminic hydrogens were located and refined using distance restraints for **2** and **4**. Other hydrogen atoms were included using a riding model. Further crystal data are given in Table 1.

Special Details of Refinement. **3**: The structure contains two poorly resolved molecules of dichloromethane, of which one is disordered over an inversion center. The composition and derived parameters are based on full occupation of these sites. **7**: The structure contains three dichloromethane sites, two of which are disordered over an inversion center and are poorly defined. The composition and derived parameters are based on two dichloromethane molecules per molecule of complex. Most major features of residual electron density are in the solvent region.

Table 1. Details of Data Collection and Structure Refinement for Complexes **2** and **3**

	compd	
	2	**3**
chem formula	$C_{30}H_{16}AuClF_{10}NP$	$C_{31.5}H_{19}AuCl_4F_{10}NO_4P$
cryst habit	colorless trapezoid	colorless prism
cryst size/mm	0.40 × 0.40 × 0.30	0.36 × 0.18 × 0.10
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.8992(8)	9.241(2)
b/Å	11.828(2)	13.752(2)
c/Å	13.672(2)	15.6517(10)
α/deg	110.194(16)	100.404(10)
β/deg	97.087(14)	102.338(10)
γ/deg	106.108(12)	101.282(10)
V/Å^3	1400.1(4)	1853.5(5)
Z	2	2
D_c/g cm^{-3}	2.002	1.855
M	843.82	1035.21
F(000)	808	998
T/°C	−100	−100
$2\theta_{max}$/deg	50	56
μ(Mo Kα)/mm^{-1}	5.497	4.387
Transm	0.979, 0.522	0.999, 0.589
no. of reflcns measd	4975	12 666
no. of unique reflcns	4759	8884
R_{int}	0.0199	0.0383
R^a ($F > 4\sigma(F)$)	0.0225	0.0498
wR^b (F^2, all reflcns)	0.0536	0.1244
no. of reflcns used	4759	8884
no. of params	403	457
No. of restraints	374	129
S^c	1.036	0.996
max $\Delta\rho$/e Å^{-3}	0.979	1.742

	compd	
	4	**7**
chem formula	$C_{30}H_{15}AuF_{10}NP$	$C_{68}H_{48}Au_3Cl_5F_{10}NO_4P_3$
cryst habit	yellow tapering prism	yellow prism
cryst size/mm	0.22 × 0.15 × 0.12	0.32 × 0.16 × 0.09
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.0862(8)	13.4946(12)
b/Å	14.8036(12)	14.2351(12)
c/Å	19.3597(16)	18.5302(16)
α/deg	99.163(3)	77.029(3)
β/deg	98.068(3)	84.443(3)
γ/deg	104.580(3)	83.508(3)
V/Å^3	2712.2(4)	3437.1(5)
Z	4	2
D_c/g cm^{-3}	1.977	1.927
M	807.37	1994.13
F(000)	1544	1904
T/°C	−130	−130
$2\theta_{max}$/deg	60	60
μ(Mo Kα)/mm^{-1}	5.575	6.726
transm	0.945, 0.683	0.862, 0.555
no. of reflcns measd	29 022	59 536
no. of unique reflcns	15 390	19 933
R_{int}	0.0466	0.0459
R^a ($F > 4\sigma(F)$)	0.0349	0.0227
wR^b (F^2, all reflcns)	0.0617	0.0651
no. of reflcns used	15 390	19 933
no. of params	783	864
no. of restraints	737	296
S^c	0.802	1.034
max $\Delta\rho$/e Å^{-3}	1.514	2.190

[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.

Results and Discussion

As mentioned above, only a few gold(I) complexes containing the N,P-donor ligand PNH_2 have been reported to date,[12] and no gold(III) complex at all; our first objective was thus the synthesis of compounds of this type. Accordingly, treatment of

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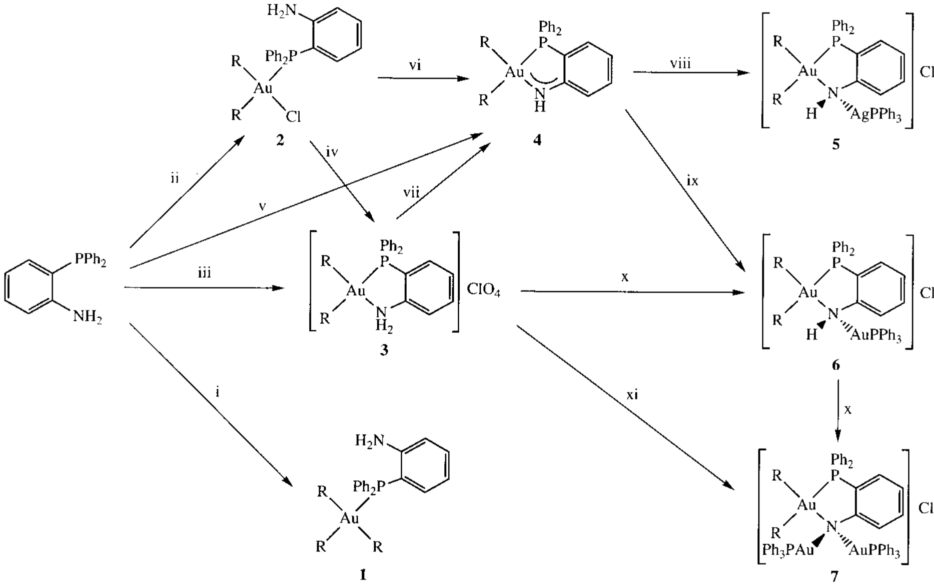
Scheme 1[a]



[a] R = C_6F_5. Key: (i) [AuR$_3$(tht)]; (ii) 1/2 [AuR$_2$(μ-Cl)]$_2$; (iii) [AuR$_2$(OEt$_2$)$_2$]ClO$_4$; (iv) AgClO$_4$; (v) [AuR$_2$(acac)]; (vi) Tl(acac); (vii) PPN(acac); (viii) [Ag(OClO$_3$)(PPh$_3$)]; (ix) [Au(OClO$_3$)(PPh$_3$)]; (x) [Au(acac)(PPh$_3$)]; (xi) 2 [Au(acac)(PPh$_3$)].

PNH$_2$ with the gold(III) starting materials [Au(C_6F_5)$_3$(tht)] or [Au(C_6F_5)$_2$(μ-Cl)]$_2$ in the appropriate molar ratio, as illustrated in Scheme 1, leads to the synthesis of the neutral gold(III) complexes [Au(C_6F_5)$_3$(PNH$_2$)] (**1**) or [Au(C_6F_5)$_2$Cl(PNH$_2$)] (**2**), in each of which the ligand is monodentate, coordinating the gold center through the phosphorus atom.

Complexes **1** and **2** are air- and moisture-stable solids, soluble in most common organic solvents and insoluble in hexane, with elemental analyses and physical and spectroscopic properties in accordance with the proposed stoichiometry. Their IR spectra show the ν(N−H) stretching absorptions at 3380 and 3460 (**1**) and 3370 and 3472 (**2**) cm^{-1} and also bands assignable to the pentafluorophenyl groups bonded to gold(III).[30,31]

The ^{31}P{^{1}H} NMR spectra show a single resonance at 12.0 (**1**) or 20.7 (**2**) ppm that appears as a multiplet because of coupling with fluorine. In the ^{19}F NMR two groups of signals, each corresponding to one type of pentafluorophenyl group, are observed with relative intensities 2:1 (**1**) or 1:1 (**2**), confirming their cis disposition. The resonance of the aminic protons appears in the ^{1}H NMR at 3.8 (**1**) or 3.9 (**2**) ppm. Finally, the peak from the molecular ion is observed in the mass spectrum of **1** (FAB+) at m/z = 975 (3%) with an experimental isotopic distribution in accordance with calculation. Other peaks corresponding to various fragments are also found: [Au(C_6F_5)$_2$(PNH$_2$)]$^+$, [Au(C_6F_5)(PNH$_2$)]$^+$, and [Au(PNH$_2$)]$^+$ at m/z = 808 (50), 641 (100), and 474 (70%) in **1** or [Au(C_6F_5)$_2$(PNH$_2$)]$^+$ and [Au(PNH$_2$)]$^+$ at m/z = 808 (65) and 474 (100%) in **2**.

The crystal structure of **2** was determined by X-ray diffraction studies on a crystal obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. The gold center is coordinated by the ipso carbon atoms of two pentafluorophenyl rings, one chlorine, and the phosphorus atom of the PNH$_2$ ligand (Figure 1) and exhibits a square planar geometry with angles from 86.09(14) to 93.32(10)° (a selection of bond lengths and angles is shown in Table 2). The greater trans influence of the PNH$_2$ ligand, compared with chlorine, is reflected in the Au−C distances. The bond trans to chlorine is 2.038(4) Å, whereas that trans to PNH$_2$ is 2.068(4) Å. There are few examples in the literature of gold(III) centers coordinated by two carbon atoms, a chlorine, and a P donor atom. The distances found in **2** compare reasonably well with those found in [Cl(C_6F_5)$_2$Au{Ph$_2$PCH(AuNC$_5$H$_5$)PPh$_2$}AuCl][38] (2.037(18), 2.052(20) Å) and [AuCl(CH$_3$)$_2${Ph$_2$PCH$_2$PPh$_2$O}][39] (2.042(5), 2.070(5) Å). The longer of the distances mentioned above are in the range of values found in tris(pentafluorophenyl) gold derivatives.[40] The Au−Cl distance is (2.3230(11) Å), shorter than in [Cl(C_6F_5)$_2$Au{Ph$_2$PCH(AuNC$_5$H$_5$)PPh$_2$}AuCl][38] (2.337(8) Å), [AuCl(CH$_3$)$_2${Ph$_2$PCH$_2$PPh$_2$O}][39] (2.391(1) Å), and [AuCl$_3$(PPh$_3$)][41] (2.347(4) Å for the chlorine trans to the triphenylphosphine; cf. 2.273(4) and 2.282(2) Å for the mutually trans chorine atoms) but longer than the bond trans to N in [AuCl$_3$(C_6H_7NO)][42] (2.265(3)−2.278(4) Å). It resembles the distances

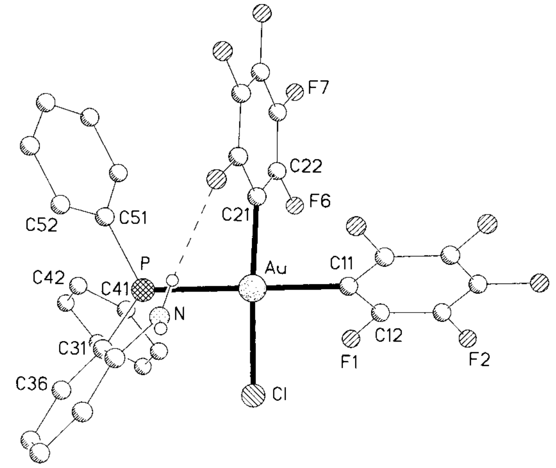


Figure 1. Structure of compound **2** in the crystal showing the atom numbering scheme. Radii are arbitrary. For clarity, only the aminic H atoms are shown.

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Table 2. Bond Lengths (Å) and Angles (deg) for **2**

Au−C(21)	2.038(4)	N−C(32)	1.383(5)
Au−C(11)	2.068(4)	C(31)−C(36)	1.402(5)
Au−Cl	2.3230(11)	C(31)−C(32)	1.411(5)
Au−P	2.3853(10)	C(32)−C(33)	1.390(6)
P−C(31)	1.812(4)	C(33)−C(34)	1.378(6)
P−C(51)	1.821(4)	C(34)−C(35)	1.382(6)
P−C(41)	1.819(4)	C(35)−C(36)	1.370(5)
C(21)−Au−C(11)	86.09(14)	C(36)−C(31)−P	119.1(3)
C(21)−Au−Cl	176.53(10)	C(32)−C(31)−P	121.6(3)
C(11)−Au−Cl	90.84(10)	N−C(32)−C(33)	119.3(4)
C(21)−Au−P	93.32(10)	N−C(32)−C(31)	122.1(4)
C(11)−Au−P	176.96(10)	C(33)−C(32)−C(31)	118.6(4)
Cl−Au−P	89.83(4)	C(34)−C(33)−C(32)	121.0(4)
C(31)−P−C(51)	108.77(17)	C(33)−C(34)−C(35)	120.5(4)
C(31)−P−C(41)	105.44(17)	C(36)−C(35)−C(34)	119.7(4)
C(51)−P−C(41)	104.75(17)	C(35)−C(36)−C(31)	121.0(4)
C(31)−P−Au	112.31(13)	C(46)−C(41)−P	119.6(3)
C(51)−P−Au	114.21(12)	C(42)−C(41)−P	120.4(3)
C(41)−P−Au	110.74(12)	C(56)−C(51)−P	118.7(3)
C(16)−C(11)−Au	122.6(3)	C(52)−C(51)−P	121.5(3)
C(12)−C(11)−Au	121.8(3)		

(2.324(2), 2.325(2) Å) trans to S found in [Ph_3PNPPh_3][Au($S_2C_2B_{10}$)Cl_2].[43] A longer Au−P distance (2.3853(10) Å) is found in **2**, compared with other phosphinogold(III) complexes, such as [Me-C_6H_3{$NHPPh_2Au(C_6F_5)_3$}$_2$] (2.346(2), 2.358(3) Å),[40] NBu_4[{$Au(C_6F_5)_3(PPh_2CHPPh_2)$}$_2$Au][44] (2.367(2) Å), or [$AuMe_3PPh_3$][45] (2.347(6) Å). It is similar to that observed in [C_6H_4{$NHPh_2Au(C_6F_5)_3$}{N($AuPPh_3$)$PPh_2Au(C_6F_5)_3$}] (2.3829(15), 2.3615(16) Å).[40]

The C(31)−C(32) distance between the two carbons of the PNH_2 skeleton is 1.411(5) Å. The amine group forms an intramolecular hydrogen bond to a fluorine atom: N−H02···F10, with H···F 2.30(4) Å and N−H···F 161(4)°.

In complexes **1** and **2** the ligand is monodentate, but it can also behave as bidentate chelating ligand when treated with equimolecular amounts of [$Au(C_6F_5)_2(OEt_2)_2$]ClO_4. This reaction leads to the new cationic complex [$Au(C_6F_5)_2(PNH_2)$]ClO_4 (**3**), which is soluble in chlorinated solvents and acetone and insoluble in diethyl ether and hexane. It behaves as a uni-univalent electrolyte in acetone solutions, and its elemental analysis and spectroscopic properties agree with the proposed stoichiometry.

The infrared spectrum of **3** displays a broad band at ∼3520 cm^{-1} from the NH_2 group and bands from the perfluorophenyl groups similar to those observed in **2,** besides bands from the anion at ∼1100 (vs, br) and 623 (m) cm^{-1}.[46] The $^{31}P\{^1H\}$ NMR signal of the ligand is located at 45.1 ppm. The ^{19}F NMR of **3** is similar to that registered for complex **2,** and in its mass spectrum (FAB+) the peak corresponding to the molecular cation appears at $m/z = 808$ (87%), while the largest peak located at $m/z = 474$ corresponds to the fragment [$Au(PNH_2)$]$^+$.

The neutral amido complex [$Au(C_6F_5)_2(PNH)$] (**4**) can be obtained by deprotonation of **3** with PPN(acac) or by treatment of the chloro complex **2** with Tl(acac). Furthermore, reaction of the free ligand with the (acetylacetonato)gold(III) derivative [$Au(C_6F_5)_2$(acac)] also leads to the synthesis of **4** through an alternative pathway (see Scheme 1). This complex is obtained as a stable yellow solid, soluble in most common organic solvents and insoluble in hexane. Its physical, analytical, and spectroscopic properties agree with the proposed stoichiometry.

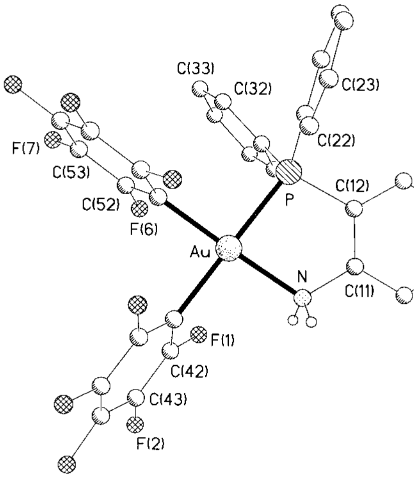

Figure 2. Structure of the cation of compound **3** in the crystal showing the atom numbering scheme. Radii are arbitrary. For clarity, only the aminic H atoms are shown.

In the IR spectrum of **4**, apart from the absorptions from the perfluorophenyl groups, a sharp band at 3409 cm^{-1} is now observed arising from the NH group. Compared with **3**, the resonance of the phosphorus atom appears in its $^{31}P\{^1H\}$ NMR at higher field because of the deprotonation of the NH_2 group. This effect is also shown in the ^1H NMR spectrum, where the signal of the NH is now located at 5.19 ppm. In its mass spectrum (FAB+) the parent peak at $m/z = 807$ corresponds to M^+.

To determine the structural differences between **3** and **4**, single crystals of both complexes were grown by diffusion of hexane in a solution of the respective complex in dichloromethane and their crystal structures were determined by X-ray diffraction.

Compound **3** contains one independent formula unit in the unit cell, whereas compound **4** contains two independent molecules. In both complexes the gold atoms are bonded to two pentafluorophenyl rings and chelated by the PNH_2 (**3**) or [PNH]$^-$ (**4**) ligands. The gold centers lie in the plane formed by the four donor atoms and exhibit square planar geometries (Figures 2 and 3). The narrowest angle is always that restricted by the chelating ligand (see the selection of angles and bond lengths in Tables 3 (compound **3**) and 4 (compound **4**)).The distances Au−C are 2.019(6), 2.073(7) Å in **3** and 2.041(4), 2.067(4) Å for one of the molecules in **4** and 2.053(4), 2.050(5) Å in the other. The values in **3** clearly indicate a higher trans effect of the PPh_2 group than the NH_2 group. In compound **4** the Au−C distances are more similar, indicating a higher trans effect from the deprotonated NH group than from NH_2. The additional electron density delocalized through the Au−N−C bonds is reflected in both the Au−N and N−C distances. The Au−N distance in **3** is 2.107(5) Å, whereas those found in **4** are 2.028(4), 2.024(4) Å. Similarly, the N−C distance in **3** is 1.474(9) Å, whereas those found in **4** are shorter, 1.356(6), 1.359(6) Å. No noticeable differences are observed in the C−C bond lengths between the carbon atoms bonded to the donor atoms (P and N) in the PNH_2 or [PNH]$^-$ ligands when comparing both structures or compared with **2**. The Au−P distances (2.3222(18) Å in **3**, 2.3254(13), 2.3174(13) Å in **4**) are shorter than those found for **2**. In **3** the Au−N bond distances compare well with those found in the derivatives [$Au(C_6F_5)_2$-

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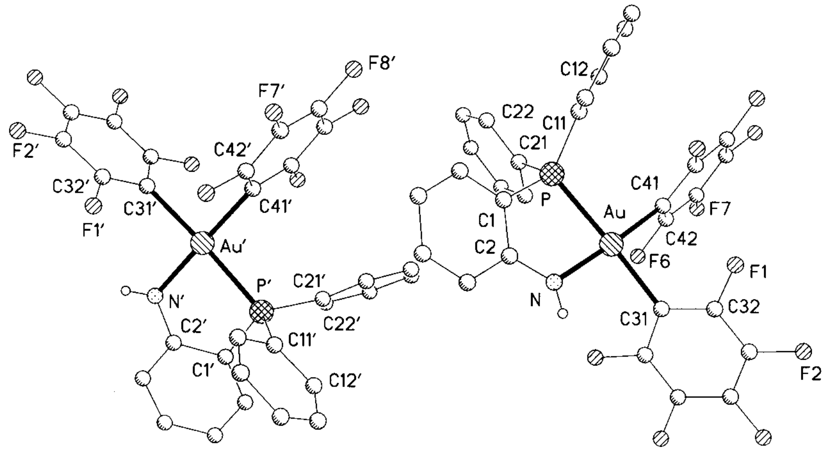

Figure 3. Structure of compound **4** in the crystal showing the atom numbering scheme. Radii are arbitrary. For clarity, only the aminic H atom is shown.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

Au−C(51)	2.019(6)	P−C(31)	1.797(7)
Au−C(41)	2.073(7)	P−C(12)	1.798(7)
Au−N	2.107(5)	P−C(21)	1.803(7)
Au−P	2.3222(18)	N−C(11)	1.474(9)
C(51)−Au−C(41)	88.6(2)	C(31)−P−C(21)	110.3(3)
C(51)−Au−N	177.0(2)	C(12)−P−C(21)	108.2(3)
C(41)−Au−N	93.5(2)	C(31)−P−Au	106.9(2)
C(51)−Au−P	92.90(18)	C(12)−P−Au	100.3(2)
C(41)−Au−P	172.17(19)	C(21)−P−Au	121.2(2)
N−Au−P	84.81(16)	C(11)−N−Au	116.6(4)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4**

Au−N	2.028(4)	Au′−N′	2.024(4)
Au−C(41)	2.041(4)	Au′−C(31′)	2.050(5)
Au−C(31)	2.067(4)	Au′−C(41′)	2.053(4)
Au−P	2.3254(13)	Au′−P′	2.3174(13)
P−C(1)	1.786(4)	P′−C(1′)	1.791(4)
P−C(11)	1.792(4)	P′−C(21′)	1.803(5)
P−C(21)	1.803(4)	P′−C(11′)	1.805(4)
N−C(2)	1.356(6)	N′−C(2′)	1.359(6)
N−Au−C(41)	176.70(17)	N′-Au′−C(31′)	91.25(17)
N−Au−C(31)	94.10(16)	N′−Au′−C(41′)	178.91(17)
C(41)−Au−C(31)	88.42(15)	C(31′)−Au′−C(41′)	89.77(16)
N−Au−P	82.09(13)	N′−Au′−P′	82.98(13)
C(41)−Au−P	95.44(12)	C(31′)−Au′−P′	173.01(12)
C(31)−Au−P	175.99(11)	C(41′)−Au′−P′	96.04(12)
C(1)−P−C(11)	110.2(2)	C(1′)−P′−C(21′)	109.8(2)
C(1)−P−C(21)	108.9(2)	C(1′)−P′−C(11′)	105.96(19)
C(11)−P−C(21)	106.96(19)	C(21′)−P′−C(11′)	108.5(2)
C(1)−P−Au	100.42(16)	C(1′)−P′−Au′	99.54(16)
C(11)−P−Au	116.92(15)	C(21′)-P′−Au′	114.72(15)
C(21)−P−Au	113.18(15)	C(11′)−P′−Au′	117.42(15)
C(2)−N−Au	122.0(3)	C(2′)−N′−Au′	121.2(3)

(Fcpy)$_2$]ClO$_4$ (2.076(7), 2.089(7) Å) and [$Au(C_6F_5)_3$(Fcpy)][47] (2.101(3) Å). A longer bond was found in [Au(TPB)Me$_2$][48] (TPB = 3,7-dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]-nonane) (2.22(1) Å, in which the gold center is chelated by the phosphabicyclo derivative). Shorter distances have been found in other pyridine derivatives, such us [Au{dpk-(OH)$_2$}-Cl$_2$]Cl (dpk = di-2-pyridylmethanediol-*N*,*N*′)[49] (2.039(5), 2.042(5) Å) or in [$AuCl_3(C_6H_7NO)$][42] (2.021(9) Å) and in compounds in which 2,6-diphenylpyridine (DDPY) is coordinated to the gold center through the nitrogen and two carbon atoms [Au(DPPY)-(PPh$_3$)], [Au$_2$(DPPY)$_2$(dppm)], and [Au(DPPY)(dppe)][50] (dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane) (distances between 2.019(16) and 2.040(1) Å).

As mentioned above, we were especially interested in the synthesis of mixed gold(III)−M(I) compounds, to determine whether metal−metal contacts can also appear in such compounds. Thus, we treated the neutral derivative **4** with [Ag-(OClO$_3$)(PPh$_3$)] or with a freshly prepared solution of [Au-(PPh$_3$)]ClO$_4$ (1:1), isolating the new cationic complexes [$Au(C_6F_5)_2$\{PNH(MPPh$_3$)\}]ClO$_4$ (M = Ag (**5**), Au (**6**)). Complex **6** can also be obtained by direct reaction of **3** with an equimolecular amount of [Au(acac)(PPh$_3$)]. These species are obtained as yellow (**5**) or orange (**6**) air- and moisture-stable solids, soluble in chlorinated solvents and acetone and insoluble in diethyl ether and hexane. They behave as uni-univalent electrolytes, and their analytical and spectroscopic properties agree with the proposed stoichiometry.

Their $^{31}P\{^1H\}$ NMR spectra display a new resonance from the PPh$_3$ bonded to the M(I) center. In the case of silver this signal appears at room temperature as a doublet of multiplets centered at 14.1 ppm that splits into a doublet of doublets centered at 13.0 ppm when the temperature is decreased to 223 K. This pattern is due to the coupling of the phosphorus atom of the triphenylphosphine ligand with both NMR-active isotopomers of silver (^{109}Ag and ^{107}Ag) with coupling constants of 803 (^{109}Ag−P) and 691 (^{107}Ag−P) Hz. In the $^{31}P\{^1H\}$ NMR of **6** the resonance of the PPh$_3$ ligand is located at 29.3 ppm. The phosphorus of the PPh$_2$ group appears at 45.2 (**5**) or 42.4 (**6**) ppm.

Similarly to our observations in the ^{1}H NMR spectrum of **3**, the resonance of the aminic proton seems to be masked by those corresponding to the aromatic protons in these two complexes, while the ^{19}F NMR is similar to that registered for **3**.

Finally, the peak due to the molecular cation is observed in the mass spectra (ES+) at *m*/*z* = 1177 (7, **5**) or 1266 (95%, **6**). These spectra also display other peaks corresponding to the fragments [AgPPh$_3$]$^+$ or [PNH(AuPPh$_3$)]$^+$ at *m*/*z* = 670 (45, **5**) or 736 (50%, **6**), respectively.

Both protons of the PNH$_2$ ligand can be replaced by AuPPh$_3$ groups, and thus the trinuclear complex [$Au(C_6F_5)_2$\{PN-(AuPPh$_3$)$_2$\}]ClO$_4$ (**7**) was obtained by reaction of **3** with [Au-(acac)(PPh$_3$)] (1:2) in dichloromethane or by treatment of **6** with

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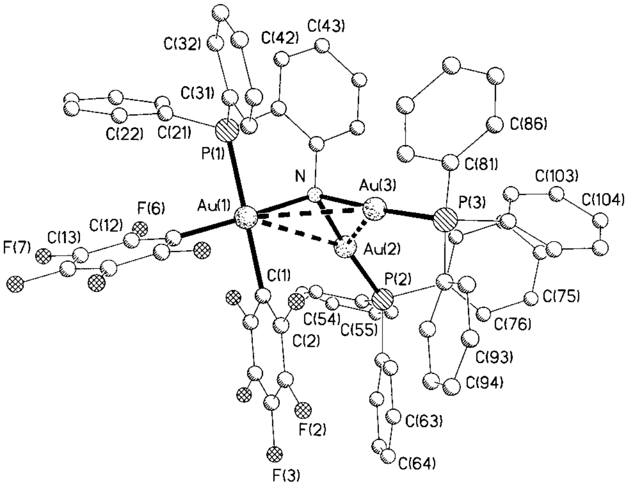

Figure 4. Structure of the cation of compound **7** in the crystal showing the atom numbering scheme. Radii are arbitrary. H atoms are omitted for clarity.

an equimolecular amount of the same acetylacetonate derivative. This complex is obtained as a yellow solid with physical properties similar to those observed for **6** and analytical data in accordance with the proposed stoichiometry.

The $^{31}P\{^{1}H\}$ NMR spectrum of **7** shows two resonances at 46.3 (PPh_2) and 27.5 ($AuPPh_3$) ppm, the latter with a higher intensity, while in its ^{1}H NMR spectrum only signals due to aromatic protons are observed. The peak corresponding to the molecular cation also appears in the mass spectrum (ES+) of **7** at $m/z = 1725$ (16%).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **7**

Au(1)−C(11)	2.046(3)	Au(2)−P(2)	2.2395(9)
Au(1)−N	2.079(3)	Au(2)−Au(3)	2.9749(3)
Au(1)−C(1)	2.088(4)	Au(3)−N	2.104(3)
Au(1)−P(1)	2.3113(9)	Au(3)−P(3)	2.2505(9)
Au(1)−Au(3)	3.3219(3)	P(1)−C(41)	1.790(3)
Au(2)−N	2.077(3)	N−C(46)	1.438(4)

C(11)−Au(1)−N	176.81(12)	P(3)−Au(3)−Au(1)	145.15(3)
C(11)−Au(1)−C(1)	87.07(13)	Au(2)−Au(3)−Au(1)	67.190(8)
N−Au(1)−C(1)	95.03(12)	C(41)−P(1)−Au(1)	100.33(12)
C(11)−Au(1)−P(1)	93.39(9)	C(21)−P(1)−Au(1)	115.46(11)
N−Au(1)−P(1)	84.47(8)	C(31)−P(1)−Au(1)	113.34(12)
C(1)−Au(1)−P(1)	179.12(10)	C(61)−P(2)−Au(2)	111.91(11)
C(11)−Au(1)−Au(3)	145.26(9)	C(51)−P(2)−Au(2)	116.96(11)
N−Au(1)−Au(3)	37.68(7)	C(71)−P(2)−Au(2)	108.04(11)
C(1)−Au(1)−Au(3)	82.50(9)	C(91)−P(3)−Au(3)	115.42(13)
P(1)−Au(1)−Au(3)	97.52(2)	C(101)−P(3)−Au(3)	112.42(12)
N−Au(2)−P(2)	174.17(7)	C(81)−P(3)−Au(3)	109.89(12)
N−Au(2)−Au(3)	44.99(7)	C(46)−N−Au(2)	116.5(2)
P(2)−Au(2)−Au(3)	129.33(2)	C(46)−N−Au(1)	116.0(2)
N−Au(3)−P(3)	176.53(8)	Au(2)−N−Au(1)	114.51(12)
N−Au(3)−Au(2)	44.29(7)	C(46)−N−Au(3)	110.14(18)
P(3)−Au(3)−Au(2)	136.84(3)	Au(2)−N−Au(3)	90.72(10)
N−Au(3)−Au(1)	37.17(7)	Au(1)−N−Au(3)	105.15(12)

Finally, X-ray diffraction studies were carried out on a single crystal of **7** grown by slow diffusion of *n*-heptane in a solution of **7** in dichloromethane. The molecule involves a $[PN]^{2-}$ ligand that chelates a gold(III) center, also bonded to two pentafluorophenyl rings. The nitrogen atom is also bonded to two $AuPPh_3$ fragments (Figure 4) resembling the structure found in the trinuclear complex of 8-aminoquinoline.[51] The gold(III) center exhibits the usual square planar geometry. As seen in complexes **2**−**4**, the narrowest angle is, once again, that restricted by the bite angle of the ligand (N−Au(1)−P(1) 84.47(8)°) (see Table 5). Linear geometry at both gold(I) centers is observed, with N−Au(2)−P(2) 174.17(7)° and N−Au(3)−P(3) 176.53(8)°. An intramolecular interaction between the two gold(I) centers (Au(2)−Au(3) 2.9749(3) Å) is present. The Au(I)−Au(III) distances (Au(1)−Au(2) 3.4961(3) Å, Au(1)−Au(3) 3.3219(3) Å) are noteworthy and may indicate the presence of weak interactions between the gold(I) and gold(III) centers. We have previously drawn attention to this possibility, as indicated by short gold(I)−gold(III) distances in some of our complexes and also by theoretical studies.[26,52] The difference in the Au−C bond lengths is appreciable (2.046(3), 2.088(4) Å), with the longer bond trans to the phosphorus atom. This situation resembles that found in **3**. The Au(III)−N (2.079(3) Å) and Au(III)−P (2.3113(9) Å) bond distances are similar to those found in **3**.

Acknowledgment. We thank the Dirección General de Enseñanza Superior (Grant No. PB97-1010-C02-02), the Fonds der Chemischen Industrie, and the CAI (Caja de Ahorros de la Inmaculada) for financial support.

Supporting Information Available: CIF files of crystal data, data collection and solution and refinement parameters, bond distances and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0100875

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