Organometallics **2002,** *21,* 2426−2429

A Pentanuclear Mixed Gold(III)−Silver(I) Phosphide with an Unusual T-Frame μ_3-Cl Bridge

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Received February 20, 2002

The reaction of the mixed gold(III)−silver(I) diphenylphosphide complex $[Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Ag]_2$ (**1**) with an equimolecular amount of $[AgCl(PPh_3)_2]$ leads to the formal insertion of the latter into **1**, affording the pentanuclear derivative $[\{Au(C_6F_5)_2\{(\mu\text{-}PPh_2)AgPPh_3\}(\mu\text{-}PPh_2)\}_2(\mu\text{-}Ag)(\mu_3\text{-}Cl)]$ (**2**). Surprisingly, complex **2** is also obtained by treatment of $[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$ with $[Ag(TfO)(PPh_3)]$ (TfO = trifluoromethanesulfonate) and AgTfO (2:2:1) in the presence of PPN(acac) (PPN = $[N(PPh_3)_2]^+$, acac = acetylacetonate) and PPNCl. The crystal structure of **2** has been determined by X-ray diffraction studies, and it displays an unusual, perfectly planar T-frame μ_3-Cl atom acting as a bridge between the three silver atoms.

Introduction

Although in the past few years a very rich chemistry of phosphido-bridged transition-metal complexes has been developed for metals of groups 8,[1] 9,[2] and 10,[3] the chemistry of gold phosphides has experienced less progress since $[\{AuPPh_2\}_n]$ was first described in 1976.[4] Thus, when we started our research in this field, only a few gold(I) species containing PR_2H[5] or PR_2^- [4−6] ligands and the dinuclear gold(III) derivative $[Au_2Me_4(\mu\text{-}PPh_2)_2]$[4] were known.

On the other hand, the synthesis and catalytic behavior of phosphido-bridged di- and polynuclear complexes continues to attract much attention.[7] We have recently reported the synthesis of a number of di-, tri-, and tetranuclear Au(III) and Au(III)−M(I) (M = Cu, Ag, Au) phosphido-bridged derivatives.[8] We have now succeeded in synthesizing a pentanuclear mixed gold(III)−silver(I) phosphide which displays an unusual, perfectly planar T-frame μ_3-Cl bridge between the silver centers.

Results and Discussion

By reacting the tetranuclear species $[Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Ag]_2$ (**1**) with an equimolecular amount of $[AgCl(PPh_3)_2]$, the complex $[\{Au(C_6F_5)_2\{(\mu\text{-}PPh_2)AgPPh_3\}(\mu\text{-}PPh_2)\}_2(\mu\text{-}Ag)(\mu_3\text{-}Cl)]$ (**2**) was obtained as shown in Scheme 1. In accordance with this preparation pathway, complex **2** can be viewed as a formal insertion product of 1 equiv of $[AgCl(PPh_3)_2]$ into the starting compound **1**, whose synthesis and crystal structure have previously been described in one of our recent papers.[8c] This reaction takes place with the concomitant breaking of

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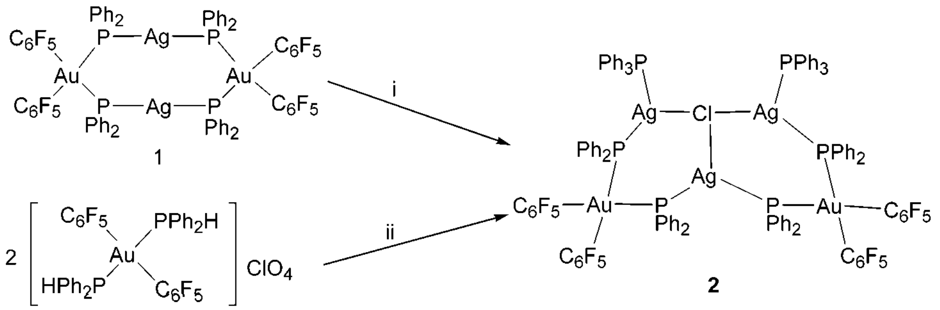
10.1021/om020142x CCC: \$22.00
Publication on Web 05/14/2002

Scheme 1[a]



[a] Legend: (i) [AgCl(PPh$_3$)$_2$]; (ii) 2 [Ag(TfO)(PPh$_3$)] + AgTfO + 4 PPN(acac) + PPNCl.

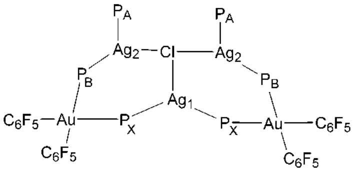


Figure 1. Schematic representation of complex **2**.

two Ag−P bonds and the reorganization of the ligands. Interesting and surprisingly, an alternative synthetic pathway is the treatment of the gold(III) phosphine derivative [Au(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$]ClO$_4$ with [Ag(TfO)(PPh$_3$)] (TfO = trifluoromethylsulfonate) and AgTfO (2:2:1) in the presence of PPN(acac) (PPN = [N(PPh$_3$)$_2$]$^+$, acac = CH(COCH$_3$)$_2$$^-$) as deprotonating agent and PPNCl. Complex **2** is obtained as a white solid with analytical data in accordance with the proposed stoichiometry. It is soluble in most common organic solvents and insoluble in hexane, and it is nonconducting in acetone solution.

Its ^{31}P{^{1}H} NMR spectrum in acetone at room temperature shows a complex set of signals between 5 and 20 ppm. When the temperature is decreased to 223 K, the spectrum is still complicated, but two doublets centered at 9.0 ppm are now observed, arising from the phosphorus P$_X$ (see Figure 1) coupled with the magnetically active ^{107}Ag and ^{109}Ag isotopes of the silver atom Ag(1) (^1J(P,^{109}Ag) = 364.5, ^1J(P,^{107}Ag) = 318.4 Hz). This spectrum also displays four broad signals located at ~17, ~13, ~9.5, and ~6 ppm, which look like an AB system and are assigned to the P$_A$ and P$_B$ atoms, which are also coupled with the magnetically active ^{107}Ag and ^{109}Ag isotopes of the Ag(2) atoms. The ^{19}F NMR spectrum of **1** is in accordance with the proposed structure, displaying two types of C$_6$F$_5$ groups bonded to gold(III), and its ^{1}H NMR spectrum only shows resonances from aromatic protons.

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of **2** in chloroform. The molecule, which displays crystallographic 2-fold symmetry, contains three silver and two gold centers. The geometry may be described as two "[(C$_6$F$_5$)$_2$Au(μ-PPh$_2$)$_2$Ag{Ag(PPh$_3$)}]" units, which share the silver atom Ag(1) (on the 2-fold axis) not coordinated to PPh$_3$. Additionally, the three silver atoms are bridged by one chloride ligand, also lying on the 2-fold axis (Figure 2). The result is a 10-membered ring in which the two central atoms are connected; the conformation could be described as twisted via the internal connection Ag(1)−Cl. Crystal structures containing "AgP−M−PAg" units have only been described for M = Ag[9] and in the

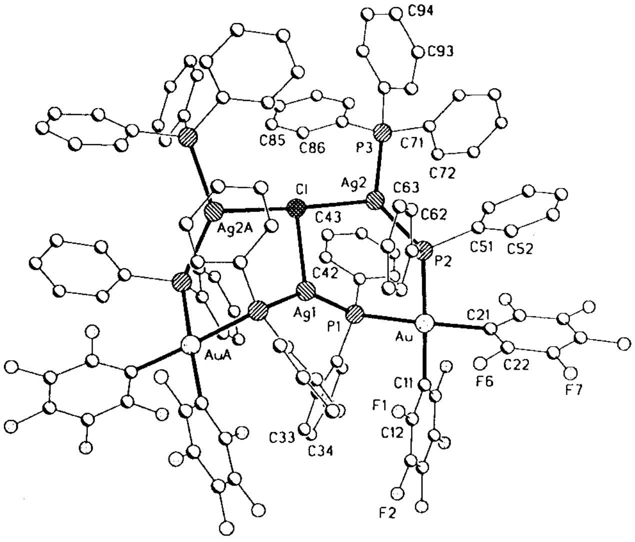


Figure 2. Molecular structure of **2**. The molecule lies on a 2-fold axis coincident with the Cl−Ag(1) vector. The thermal ellipsoids are drawn at the 50% level. H atoms are omitted for clarity.

case of the compound [(C$_6$F$_5$)$_2$Au(μ-PPh$_2$)$_2$Ag]$_2$ (**1**).[8c] Coordination of chloride to three or more silver atoms is known, but in most of the situations described, the geometry consists of four silver atoms and four chlorine atoms situated at the apexes of a cube,[10] with monophosphines coordinated to the silver centers. Another similar known geometry consists of three sulfur or selenide centers and a chloride, instead of four chloride ligands, and three silver centers and a molybdenum metallic center (instead of four silver centers) in the same arrangement. In these cases the molybdenum atom is doubly bonded to a sulfur or selenide and the silver centers are coordinated to monophosphines.[11] A very different arrangement presents [AgL(μ-Cl)]$_2$ units,[12] which form chains through Ag−Cl bonds. More complicated geometries have been described in which rigid

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Table 1. Crystal Data for Complex 2

chem formula	$C_{108}H_{70}Ag_3Au_2ClF_{20}P_6$
cryst habit	colorless prism
cryst size/mm	0.33 × 0.18 × 0.12
cryst syst	monoclinic
space group	$C2/c$
a/Å	29.968(2)
b/Å	21.0252(16)
c/Å	24.4546(18)
β/deg	125.322(3)
U/Å^3	12 572.1(16)
Z	4
D_c/g cm^{-3}	1.419
M_r	2686.45
F(000)	5216
T/°C	−130
$2\theta_{max}$/deg	56
μ(Mo Kα)/mm^{-1}	2.950
transmission	0.928, 0.738
no. of rflns measd	121 957
no. of unique rflns	15 603
R_{int}	0.0444
R^a ($F > 4\sigma(F)$)	0.0354
$R_w{}^b$ (F^2, all rflns)	0.1497
no. of rflns used	15 603
no. of params	632
no. of restraints	204
S^c	1.096
max $\Delta\rho$/e Å^{-3}	3.112

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 2[a]

Au−C(11)	2.081(5)	Ag(1)−Cl	2.637(2)
Au−C(21)	2.087(5)	Ag(2)−P(3)	2.4305(14)
Au−P(1)	2.3708(12)	Ag(2)−P(2)	2.4367(14)
Au−P(2)	2.3848(13)	Ag(2)−Cl	2.6461(4)

C(11)−Au−C(21)	88.46(19)	C(41)−P(1)−Ag(1)	114.11(17)
C(11)−Au−P(1)	92.36(13)	Au−P(1)−Ag(1)	113.90(5)
C(21)−Au−P(1)	176.25(16)	C(61)−P(2)−Au	106.05(16)
C(11)−Au−P(2)	177.76(14)	C(51)−P(2)−Ag(2)	107.75(16)
C(21)−Au−P(2)	92.62(14)	C(61)−P(2)−Ag(2)	107.08(16)
P(1)−Au−P(2)	86.70(4)	Au−P(2)−Ag(2)	122.22(5)
P(1)#1−Ag(1)−P(1)	147.37(7)	C(81)−P(3)−Ag(2)	114.37(17)
P(1)−Ag(1)−Cl	106.31(3)	C(91)−P(3)−Ag(2)	113.44(18)
P(3)−Ag(2)−P(2)	135.79(5)	C(71)−P(3)−Ag(2)	114.06(18)
P(3)−Ag(2)−Cl	107.48(5)	Ag(1)−Cl−Ag(2)	91.66(4)
P(2)−Ag(2)−Cl	112.00(5)	Ag(2)#1−Cl−Ag(2)	176.68(8)
C(31)−P(1)−Au	109.23(16)	C(22)−C(21)−Au	124.5(4)
C(41)−P(1)−Au	104.63(16)	C(26)−C(21)−Au	119.0(4)
C(31)−P(1)−Ag(1)	111.31(16)		

[a] Symmetry transformation used to generate equivalent atoms: (#1) $-x + 1, y, -z + {}^3/_2$.

structures that contain three or four silver atoms contain a chlorine atom "inside" the hole formed by the silver centers.[13] Also, the ion *catena*-$[Ag_{12}Cl_{18}]^{6-}$ has been described.[14] In this very different situation, the Ag−Cl−Ag angles are 91.66(4) and 176.68(8)° and the Ag−Cl distances lie between ca. 2.5 and 2.8 Å, a range that includes the distances found in **2** (2.637(2), 2.6461(4) Å). The Ag−Cl distances in the cation $[Ag_3(\mu\text{-}Cl)_2\{(PPh_2)_2CH_2\}_3]^+$, in which the three silver centers are bonded to two phosphorus atoms of different bis(diphenylphosphino)methane ligands and each chloride ligand connects the three silver atoms, are 2.838(2)−2.668(2) Å (anion $[SnPh_2Cl(ONO_2)_2]^-$)[13c] or 2.884(2)−2.632(2) Å (anion $ClO_4{}^-$).[13f] Only the shortest of these distances compare well with those found in **2**. The geometry at the silver centers Ag(2) is distorted trigonal, with the silver center 0.23 Å out of the plane formed by the two phosphorus atoms and the chlorine ligand. The Ag−P distances (2.4305(14), 2.4367(14) Å) compare well with those found in the cation $[Ag_3(\mu\text{-}Cl)_2\{(PPh_2)_2CH_2\}_3]^+$ (2.474(1)−2.453(1) Å, anion $[SnPh_2Cl(ONO_2)_2]^-$;[13c] 2.441(1)−2.464(1) Å, anion $ClO_4{}^-$)[13f] and are longer than those for **1** (linear geometry at silver, 2.383(2)−2.400(2) Å) and $PPN[\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2Ag]$[8b] (2.386(1) Å), both with an Ag−phosphide bond, or in $[Ag_4Cl_4(dppm)_2]$ (2.366(2), 2.379(2) Å),[15] which consists of two different "$Ag_2(\mu$-dppm)" units connected by two doubly bridging chloride ligands and two triply bridging chloride ligands. The environment of gold centers in **2** is square planar, with Au−C (2.081(5), 2.087(5) Å) and Au−P distances (2.3708(12), 2.3848(13) Å) in the range of those found in **1** Au−C, 2.069(9)−2.091(8) Å; Au−P, 2.368(2)−2.394(2) Å) and other bis(pentafluorophenyl) compounds.

Experimental Section

General Procedures. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5 × 10^{-4} M acetone solutions with a Jenway 4010 conductimeter. C, H analyses were carried out with a Perkin-Elmer 240C microanalyzer. ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX 300 instrument in hexadeuterioacetone solutions. Chemical shifts are quoted relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external), and H_3PO_4 (85%) (^{31}P, external). AgTfO was purchased from Aldrich, and $[Ag(TfO)(PPh_3)]$ was obtained by reaction of equimolecular amounts of $[AgCl(PPh_3)]$[16] and AgTfO. All the experiments were carried out under a nitrogen atmosphere using Schlenk techniques at room temperature and with freshly distilled solvents.

X-ray Diffraction Structure of $[\{Au(C_6F_5)_2\{(\mu\text{-}PPh_2)AgPPh_3\}(\mu\text{-}PPh_2)\}_2(\mu\text{-}Ag)(\mu_3\text{-}Cl)]$ (2). A suitable crystal of **2** was mounted in inert oil on a glass fiber and transferred to the cold gas stream of a Siemens Smart 1000 CCD diffractometer equipped with a Siemens LT-2 low-temperature attachment. Data were collected using monochromated Mo-Kα radiation (λ = 0.710 73 Å). The scan type was ω/ϕ. Absorption corrections were based on multiple scans: the program SADABS was applied. The structures were refined on F^2 using the program SHELXL-97.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Special refinement details: the structure contains

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extensive regions of badly resolved residual electron density, in which no solvent molecules could be clearly identified. For this reason no solvent was included in the refinement, and the formula and related information (M_r etc.) do not include solvent.

Crystal data are given in Table 1 and selected bond distances and angles in Table 2.

Synthesis of [{Au(C_6F_5)$_2${(μ-PPh$_2$)AgPPh$_3$}(μ-PPh$_2$)}$_2$(μ-Ag)(μ_3-Cl)] (2). Method 1. To a dichloromethane solution (20 mL) of **1**[8c] (0.2 mmol, 0.40 g) was added [AgCl(PPh$_3$)$_2$][18] (0.2 mmol, 0.13 g). After 1 h of stirring the solution was concentrated to ca. 5 mL and by addition of hexane (20 mL) precipitated complex **2** as a white solid. Yield: 0.39 g (73%).

Method 2. To a freshly prepared dichloromethane solution of [Au(C_6F_5)$_2$(PPh$_2$H)$_2$]ClO$_4$[8c] (0.2 mmol, 0.2 g) was added a diethyl ether solution (20 mL) of [Ag(TfO)(PPh$_3$)] (0.2 mmol, 0.11 g) and AgTfO (0.1 mmol, 0.03 g), and after 5 min was added PPN(acac)[19] (0.4 mmol, 0.26 g) and PPNCl (0.1 mmol, 0.06 g). After 2 h of stirring the solvents were partially evaporated and 20 mL of diethyl ether were added to precipitate the PPNTfO and PPNClO$_4$ formed during the reaction. After filtration, the resulting solution was concentrated and hexane was added to precipitate **2** as a white solid. Yield: 0.07 g (25%).$^{31}P\{^1H\}$ NMR (HDA, 223 K): δ 9.0 (d,d, 2P$_X$, $^1J(P,^{109}Ag) = 364.5$, $^1J(P,^{107}Ag) = 318.4$ Hz); $\delta_A \approx 14.5$ (AgPPh$_3$), $\delta_B \approx 8.3$ (PPh$_2$) ($J_{AB} \approx 450$ Hz). ^{19}F NMR (HDA, room temperature): δ −120.7 (m, 4F, F$_o$), −158.9 (t, 2F, $^3J(F_m,F_p) = 20.0$ Hz, F$_p$), −160.8 (m, 4F, F$_m$), −120.7 (m, 4F, F$_o$), −160.8 (t, 2F, $^3J(F_m,F_p) = 20.0$ Hz, F$_p$), −161.9 (m, 4F, F$_m$). Anal. Calcd for $C_{108}H_{70}Ag_3Au_2ClF_{20}P_6$ (2686.38): C, 48.3; H, 2.65. Found: C, 48.9; H, 2.8. $\Lambda_M = 8\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Acknowledgment. We thank the DGI (M.C.T.) (No. BQU2001-2409), the CAR (ANGI2001/28), the UR (No. API01/B14), the Fonds der Chemischen Industrie, and the CAI (Caja de Ahorros de la Inmaculada) for financial support.

Supporting Information Available: Tables of crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020142X

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