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Synthesis and Structural Characterization of Silver(I) and Gold(I) Complexes with 2-Mercaptonicotinic Acid (H_2mna) and Triphenylphosphine Ligands, and Their Antimicrobial Activities. Crystal Structures of Monomeric, 3- and 4-Coordinate Silver(I) Complexes [Ag(Hmna)(PPh$_3$)$_2$] and [Ag(Hmna)(PPh$_3$)$_3$] in the Solid State

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Two types of silver(I)-triphenylphosphine complexes with 2-mercaptonicotinic acid (H_2mna) were prepared as [Ag(Hmna)(PPh$_3$)$_n$] (**1**, $n = 2$; **2**, $n = 3$); their crystal structures determined by single-crystal X-ray diffraction. These complexes were obtained from reactions of the precursor, [Ag(Hmna)]$_n$, with less excess (3 equiv) and large excess (20 equiv) amounts of PPh$_3$, respectively. Complex **1** was also obtained from a reaction among another precursor [AgCl(PPh$_3$)$_3$], H_2mna and aqueous NaOH. The coordination geometry of **1** was a trigonal pyramid with an AgSP$_2$ core; there was a weak interaction between the silver(I) center and the pyridine nitrogen atom, while that of **2** was a distorted tetrahedron with an AgSP$_3$ core. In both **1** and **2**, the carboxyl group was protonated and its oxygen atoms did not participate in the coordination. In contrast to the formation of **1** and **2**, a related complex, [Ag(Hmba)(PPh$_3$)$_3$] **4** (H_2mba = 2-mercaptobenzoic acid), has been obtained from a reaction of [Ag(Hmba)]$_n$ with a stoichiometric amount (3 equiv) of PPh$_3$. On the other hand, the gold(I) complex, [Au(Hmna)(PPh$_3$)] **3**, with a 2-coordinate AuSP core, was prepared by a stoichiometric reaction among [AuCl(PPh$_3$)], H_2mna and aqueous NaOH. Complex **3** in the solid state showed a supramolecular array based on a repetition of hydrogen-bonding interactions between the carboxyl group and the pyridine nitrogen atom, also being contrasted to the related complex, [Au(Hmba)(PPh$_3$)] **5**, with a hydrogen-bonding dimer structure in the solid state. In CHCl$_3$, both **1** and **2** were present as several equilibrium species due to a successive dissociation of PPh$_3$ ligands, while **3** was present as an almost monomer. The antimicrobial activities in aqueous media of **1**—**5**, evaluated by minimum inhibitory concentration (MIC), were also tested.

There is currently considerable interest in the coordination chemistry of coinage metals, such as silver(I) and gold(I), with biological and/or medicinal activities.[1—7] The studies of silver(I) complexes have been mostly focused so far on their antiethylene[2a,2b] and antimicrobial activities,[2c,2d] whereas those of gold(I) complexes mostly on their antiarthritic activities,[1,3] antitumor activities,[1,4,6a] and also, recently, antimicrobial acitivities.[5,7m] In the medicinally or pharmaceutically active compounds of silver(I) and gold(I), most of the complexes formed with thiol and nitrogen-containing heterocyclic ligands are harder to crystallize and are believed to be polymeric.[1e,3g,3h,7a,7b,7c] In general, tertiary phosphine ligands have usually been employed in order to obtain crystalline compounds,[6,7f,7g,7h,7i] although several crystalline thiolatogold(I) complexes without tertiary phosphines, [Au(SR)$_2$]$^{n-}$ (HSR = thiolate), have recently been found.[7d,8] Probably, a recent development of monomeric Au^{I} compounds composed of both thiol and tertiary phosphine ligands stems from the discovery of auranofin ((2,3,4,6-tetra-*O*-acetyl-β-1-thio-D-glucopyranosato-*S*)(triethylphosphine)-gold(I)),[1,3] which has been used in chemotherapy as an effective antiarthritic agent.

We have recently prepared two types of thiolate-silver(I) complexes:[7c] a water-soluble complex, {Na[Ag(mba)]·H_2O}$_n$ (n = 21—27; H_2mba = 2-mercaptobenzoic acid, Chart 1), and a water-insoluble complex, [Ag(Hmba)]$_n$, both of which have displayed effective antimicrobial activities against selected bacteria and yeast. The former complex has been commercialized as an antimicrobial agent.[7n] The X-ray structures of both silver(I) complexes have not yet been determined.[9] On the other hand, the H_2mba li-

H_2mna H_2mba

Chart 1.

gand has given a water-soluble, crystalline gold(I) complex, $Na_3[Au(mba)_2]\cdot 5H_2O$, showing effective antiarthritic activities.[7d,7o,7p] Further, their triphenylphosphine derivatives have also recently been prepared as $[Ag(Hmba)(PPh_3)_3]$ **4** and $[Au(Hmba)(PPh_3)]$ **5**, and their X-ray structures determined.[7i] Complex **4** was a monomeric, "rigid" 4-coordinate complex with an $AgSP_3$ core in solution and in the solid state, while complex **5** with a 2-coordinate AuSP core was present as a dimer in the solid state via hydrogen-bonding interactions between the carboxyl groups. Independently, the solid state dimeric structure of **5** has also been confirmed by Tiekink et al.[6a]

As a related ligand, we selected a more versatile and polyfunctional ligand, i.e., 2-mercaptonicotinic acid (H_2mna). The present work was aimed at (1) preparing silver(I) and gold(I) complexes with H_2mna in the presence of an auxiliary ligand, PPh_3, (2) providing their X-ray crystal structures, (3) examining the effect of an aromatic nitrogen donor atom on their crystal structures, in comparison with the crystal structures of **4** and **5**, (4) clarifying their behavior in $CHCl_3$ solution, and (5) testing their bioinorganic action in aqueous media, i.e., antimicrobial activities.

Herein, we report on the full details of the synthesis and structural characterization of two novel silver(I) complexes, $[Ag(Hmna)(PPh_3)_n]$ (**1**, $n = 2$; **2**, $n = 3$), and one gold(I) complex, $[Au(Hmna)(PPh_3)]$ **3**. The solution behavior and the antimicrobial activities of these and related complexes are presented.

Results and Discussion

Compositional Characterization. The composition and molecular formula of the precursor, $[Ag(Hmna)]_n$, obtained as a yellow powdery solid sparingly soluble in DMSO, and insoluble in most solvents, except for aqueous NaOH solution, are based on elemental analyses, thermogravimetric and differential thermal analyses (TG/DTA), FT-IR, and ^1H and ^{13}C NMR in DMSO-d_6, as shown in Table 1.

Characterization data of **1**—**3** by elemental analyses, TG/DTA, solution molecular-weight measurements, FT-IR and solution NMR (^1H, ^{13}C, ^{31}P, and ^{109}Ag for **1** and **2**) spectroscopies are listed in Table 1. The composition and molecular formula of **1**—**3** are based on elemental analyses (in particular for **1**, all elements including oxygen, 99.84% total are observed), TG/DTA and single-crystal X-ray structure analyses. All of the complexes were isolated without any solvated molecules.

The solid FT-IR spectra of all complexes show the disappearance of the S–H stretching band around 2560 cm^{-1} due to the SH group in the free ligand, suggesting metal–S bond formation. Many weak bands observed in the 3000—2500 cm^{-1} region are also attributed to the presence of a protonated carboxyl group, as is usually observed.[7c,7d,7e,7k] In **3**, the carbonyl stretching band at 1703 cm^{-1} was shifted to a higher frequency region, compared with 1680 cm^{-1} found for the free ligand, which was attributed to the presence of a hydrogen-bonding interaction between the carboxyl proton and the pyridine nitrogen atom. The finding of no coordination of the carboxyl oxygen atoms in **1**—**3** and the presence of a hydrogen-bonding interaction ($O–H\cdots N$) in **3** are supported by X-ray crystallography. FT-IR measurements of **1**—**3** also confirm the presence of coordinated PPh_3 ligands as typical vibrational bands.

Synthetic Reactions and Stoichiometries. The synthetic reactions of **1**—**3** are outlined in Eqs. 1, 2, 3, and 4 (Scheme 1).

Complex **1** was prepared from two different precursors, $[Ag(Hmna)]_n$ and $[AgCl(PPh_3)_3]$, as shown in Eqs. 1 and 2, respectively.

In Eqs. 1 and 3, the actual reactions, which gave the compounds in good yields, were attained only in the presence of excess amounts of the free PPh_3 ligand; **1** was obtained under less excess PPh_3 conditions, i.e., by the $[Ag(Hmna)]_n : PPh_3 = 1:3$ molar-ratio reaction, and **2** under much more excess PPh_3 conditions, i.e., by the 1 : 20 molar-ratio reaction. The 1 : 1, 1 : 2, 1 : 5, and 1 : 10 molar-ratio reactions have also been examined and the products analyzed. In fact, the 1 : 1 and 1 : 2 molar-ratio reactions gave a mixture of **1** and unreacted $[Ag(Hmna)]_n$ and, therefore, the yield of **1**, itself, was low. The 1 : 5 molar-ratio reaction gave **1** in a relatively low yield and none of **2**. On the other hand, a 1 : 10 molar-ratio reaction gave **2** with a lower yield (see the Experimental Section).

As for Eqs. 1 and 3, it should be noted that the actual mechanism of the reaction should be much more complicated than what the apparent stoichiometries suggest. In the previously reported reaction $1/n\ [Ag(Hmba)]_n + 3PPh_3 \rightarrow [Ag(Hmba)(PPh_3)_3]$, the product was prepared using a stoichiometric amount (3 equiv) of PPh_3.[7i] The precursor, $[Ag(Hmba)]_n$, has been considered to be a cluster formed by many bridged sulfur atoms.[9] In Eqs. 1 and 3, the precursor, $[Ag(Hmna)]_n$, is considered to be a hexanuclear silver(I) cluster containing coordination by one aromatic nitrogen and two bridging sulfur atoms and silver(I)–silver(I) interactions.[7k] Thus, the presence of Ag–N bonds in $[Ag(Hmna)]_n$ and also of an intramolecular weak Ag–N interaction in **1** found in the present work may account for the requirement of excess amounts of PPh_3 for the formation of **1** and **2**, respectively.

Molecular and Crystal Structures. The molecular structures of **1** and **2** along with the atom numbering scheme are depicted in Figs. 1 and 2, respectively. Selected bond distances and angles with their estimated standard deviations are listed in Table 2. The carboxyl groups of **1** and **2** participate neither in the coordination to the silver(I) center nor in intermolecular dimerization through hydrogen bonds. Therefore, these two silver(I) complexes are discrete monomers in the crystals.

In **1**, two PPh_3 and $Hmna^-$ ligands coordinate to the silver(I) center via P1, P2, and S atoms, in which the Ag–P distances are Ag–P1 2.448(2) and Ag–P2 2.4479(8) Å, and the Ag–S distance is 2.583(2) Å. The angles of P1–Ag–P2, P1–Ag–S, and P2–Ag–S are 123.67(4), 115.61(5), and 118.87(4)°, respectively. The four atoms (P1, P2, S, and Ag) are in the plane. The Ag–N distance of **1** is 2.561(2) Å, which is longer than that of most Ag complexes; however,

Table 1. Characterization Data of the Precursor $[Ag(Hmna)]_n$ and Complexes **1**—**3**

Microanalysis	Found (Calcd)/%
$[Ag(Hmna)]_n$ ($C_6H_4NO_2SAg$)	C, 26.1 (27.5); H, 1.53 (1.54); N, 5.45 (5.35).
1[a] ($C_{42}H_{34}NO_2P_2SAg$)	C, 64.11 (64.13); H, 4.45 (4.36); N, 1.83 (1.78); O, 4.00 (4.07); P. 7.85 (7.88); S, 4.00 (4.08); Ag, 13.60 (13.71); Total, 99.84 (100).
1[b] ($C_{42}H_{34}NO_2P_2SAg$)	C, 63.82 (64.13); H, 4.10 (4.36); N, 1.73 (1.78).
2 ($C_{60}H_{49}NO_2P_3SAg$)	C, 68.73 (68.71); H, 4.77 (4.71); N, 1.70 (1.34); S, 3.15 (3.06).
3 ($C_{24}H_{19}NO_2PSAu$)	C, 46.83 (46.99); H, 3.09 (3.12); N, 2.39 (2.28); S, 5.23 (5.23).
TG/DTA data	
$[Ag(Hmna)]_n$	No weight loss before decomposition. Decomposition began around 200 °C. Exothermic peaks at 147 and 202 °C.
1[a]	No weight loss before decomposition. Decomposition began around 170 °C. Endothermic peak at 194 °C. Exothermic peak at 210 °C.
1[b]	No weight loss before decomposition. Decomposition began around 170 °C. Endothermic peak at 166 °C. Exothermic peak at 207 °C.
2	No weight loss before decomposition. Decomposition began around 154 °C. Endothermic peaks at 154, 194, and 297 °C. Exothermic peak at 230 °C.
3	No weight loss before decomposition. Decomposition began around 196 °C. Endothermic peak at 196 °C. Exothermic peak at 205 °C.
Molecular weight measurements in $CHCl_3$.	Found (Calcd)
1[a]	621 (786.6 for $[Ag(Hmna)(PPh_3)_2]$)
2	510 (1048.9 for $[Ag(Hmna)(PPh_3)_3]$)
3	655 (613.4 for $[Au(Hmna)(PPh_3)]$)
Some prominent IR bands at 1700-400 cm^{-1} region (KBr)	
$[Ag(Hmna)]_n$	1577s, 1491w, 1385vs, 1320m, 1254w, 1152w, 1046w, 800w, 737w, 642w cm^{-1}.
1[a]	1708vs, 1571m, 1542m, 1478m, 1433s, 1387s, 1132m, 1094m, 1073w, 1026w, 997w, 742m, 693s, 516m, 503m cm^{-1}.
1[b]	1709vs, 1571m, 1542m, 1479m, 1433s, 1387s, 1132m, 1094m, 1073w, 1026w, 997w, 742s, 693s, 516s, 504s cm^{-1}.
2	1709vs, 1569m, 1540w, 1478m, 1434s, 1405m, 1377m, 1269w, 1129m, 1092m, 1070w, 1026w, 998w, 743s, 694vs, 512s cm^{-1}.
3	1703m, 1577m, 1556m, 1480m, 1436s, 1386w, 1284m, 1183w, 1133m, 1101vs, 1072vs, 998m, 827m, 746s, 712s, 692vs, 539vs, 507m, 424w cm^{-1}.
^{1}H NMR	
$[Ag(Hmna)]_n$	(DMSO-d_6, 23 °C) δ = 7.54 (1H, d, H4), 6.77 (1H, dd, H5), 7.79 (1H, d, H6), 13.17 (CO_2H).
1[a]	($CDCl_3$, 23 °C) δ = 7.68 (1H, d, H4), 6.65 (1H, dd, H5), 8.22 (1H, d, H6), 7.28 (30H, m, Ph).
1[b]	($CDCl_3$, 23 °C) δ = 7.68 (1H, d, H4), 6.65 (1H, dd, H5), 8.23 (1H, d, H6), 7.30 (30H, m, Ph).
2	($CDCl_3$, 23 °C) δ = 7.67 (1H, d, H4), 6.62 (1H, dd, H5), 8.25 (1H, d, H6), 7.25 (45H, m, Ph).
3	(CD_2Cl_2, 23 °C) δ = 8.39 (1H, d, H4), 7.09 (1H, dd, H5), 8.45 (1H, d, H6), 7.47 (15H, m, Ph).
^{13}C NMR	
$[Ag(Hmna)]_n$	(DMSO-d_6, 23 °C) δ = 168.2 (C7), 161.6 (C2), 150.1 (C6), 135.6 (C4), 132.6 (C3), 118.3 (C5).
1[a]	($CDCl_3$, 23 °C) δ = 172.3 (C7), 168.0 (C2), 150.5 (C6), 140.1 (C4), 128.7 (d, J_{CP} = 9.25 Hz, Ph), 129.9 (s, Ph), 133.1 (d, J_{CP} = 20.2 Hz, Ph), 133.7 (d, J_{CP} = 16.6 Hz, Ph), 126.0 (C3), 117.0 (C5).
1[b]	($CDCl_3$, 23 °C) δ = 172.2 (C7), 167.9 (C2), 150.6 (C6), 140.1 (C4), 128.7 (d, J_{CP} = 9.25 Hz, Ph), 129.9 (s, Ph), 133.2 (d, J_{CP} = 20.3 Hz, Ph), 133.7 (d, J_{CP} = 16.6 Hz, Ph), 126.1 (C3), 117.1 (C5).
2	($CDCl_3$, 23 °C) δ = 173.3 (C7), 168.5 (C2), 150.6 (C6), 139.9 (C4), 128.6 (d, J_{CP} = 7.33 Hz, Ph), 129.6 (s, Ph), 133.8 (d, J_{CP} = 18.4 Hz, Ph), 134.0 (d, J_{CP} = 12.9 Hz, Ph), 125.8 (C3), 116.4 (C5).
3	(CD_2Cl_2, 23 °C) δ = 166.8 (C7), 164.7 (C2), 151.6 (C6), 141.1 (C4), 129.5 (d, J_{CP} = 57.0 Hz, Ph), 129.7 (d, J_{CP} = 11.0 Hz, Ph), 132.4 (s, Ph), 134.7 (d, J_{CP} = 12.9 Hz, Ph), 127.2 (C3), 120.1 (C5).
^{31}P NMR	
1[a]	($CDCl_3$, 23 °C) δ = 6.48,
1[b]	($CDCl_3$, 23 °C) δ = 6.44,
2	($CDCl_3$, 23 °C) δ = 3.27,
3	(CD_2Cl_2, 23 °C) δ = 37.2.
^{109}Ag NMR	
1[a]	($CDCl_3$, 23 °C) δ = 1055,
2	($CDCl_3$, 23 °C) δ = 1105.

a) The complex **1** prepared from polymeric precursor $[Ag(Hmna)]_n$. b) The complex **1** prepared from precursor $[AgCl(PPh_3)_3]$.

this value is shorter than the sum of the ionic radius of Ag^I (1.16 Å (4-coordinate))[10a] and the van der Waals radius of N (1.55 Å).[10b] There is probably a weak interaction between the silver(I) and N atoms. Thus, the geometry around the silver(I) atom is described to be trigonal pyramidal, rather than trigonal planar. In relation to **1**, the 3-coordinate, cationic silver(I) complex with a trigonal planar structure consisting of an $AgNP_2$ core, $[Ag(NCCH_3)(PPh_3)_2][BF_4]$

$$1/n\ [Ag(Hmna)]_n + 2PPh_3 \longrightarrow \underset{\mathbf{1}}{[Ag(Hmna)(PPh_3)_2]} \tag{1}$$

$$[AgCl(PPh_3)_3] + H_2mna + NaOH \longrightarrow \underset{\mathbf{1}}{[Ag(Hmna)(PPh_3)_2]} + PPh_3 + NaCl + H_2O \tag{2}$$

$$1/n\ [Ag(Hmna)]_n + 3PPh_3 \longrightarrow \underset{\mathbf{2}}{[Ag(Hmna)(PPh_3)_3]} \tag{3}$$

$$[AuCl(PPh_3)] + H_2mna + NaOH \longrightarrow \underset{\mathbf{3}}{[Au(Hmna)(PPh_3)]} + NaCl + H_2O \tag{4}$$

Scheme 1. Reaction schemes.

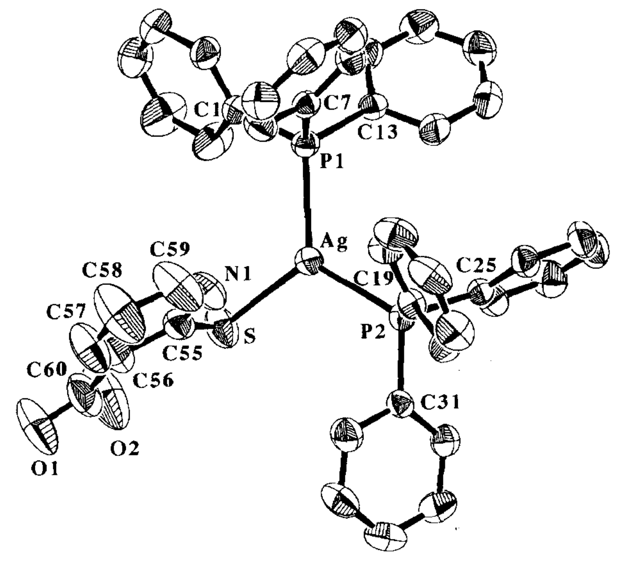

Fig. 1. Molecular structure of [Ag(Hmna)(PPh$_3$)$_2$] **1** with 50% probability ellipsoids.

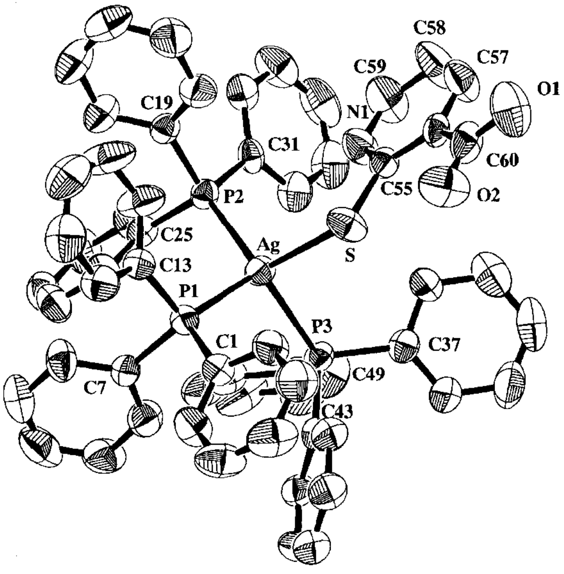

Fig. 2. Molecular structure of [Ag(Hmna)(PPh$_3$)$_3$] **2** with 50% probability ellipsoids.

(the N1–Ag1–P1, N1–Ag1–P2, and P1–Ag1–P2 angles are 116.37(6), 113.11(6), and 129.37(2)°, respectively) has been reported.[11a]

Table 2. Selected Bond Distances (Å) and Angles (°) for Complexes **1** and **2**

	1	**2**
Ag–S	2.583(2)	2.600(2)
Ag–P1	2.448(2)	2.614(7)
Ag–P2	2.4479(8)	2.543(3)
Ag–P3	—	2.570(3)
Ag···N1	2.561(2)	3.412(10)
S–Ag–P1	115.61(5)	100.24(7)
S–Ag–P2	118.87(4)	116.99(8)
S–Ag–P3	—	103.15(8)
P1–Ag–P2	123.67(4)	113.25(18)
P1–Ag–P3	—	111.19(13)
P2–Ag–P3	—	111.18(9)
Ag–S–C55	87.33(12)	109.6(2)
Ag–P1–C1	118.30(9)	118.9(2)
Ag–P1–C7	106.53(11)	111.7(2)
Ag–P1–C13	117.95(10)	115.9(2)
Ag–P2–C19	113.13(9)	115.7(2)
Ag–P2–C25	115.33(10)	112.1(2)
Ag–P2–C31	114.43(8)	118.4(2)
Ag–P3–C37	—	115.7(2)
Ag–P3–C43	—	112.4(2)
Ag–P3–C49	—	116.7(2)

In **2**, three PPh$_3$ and Hmna$^-$ ligands coordinate to the metal atom. The angles of P1–Ag–P2, P1–Ag–P3, and P1–Ag–S are 113.25(18), 111.19(13), and 100.24(7)°, respectively, indicating that the geometry around silver(I) is distorted tetrahedral. The Ag–P distances are Ag–P1 2.614(7), Ag–P2 2.543(3), and Ag–P3 2.570(3) Å, and the Ag–S distance is 2.600(2) Å. The Ag–P distances of the crowded complex **2** are longer than those of **1**. The Ag–N distance of **2** is 3.412(10) Å, indicating that there is no interaction between Ag^{I} and N atoms. Because the N atom of the Hmna$^-$ can interact with the Ag^{I} atom, as observed in **1**, excess PPh$_3$ would be necessary to form **2**. The molecular structure of **2** is compared with that of the related, distorted tetrahedral complex **4** with an AgSP$_3$ core; the Ag–S distance is 2.608(7) Å, the Ag–P1, Ag–P2, and Ag–P3 distances are 2.574(7), 2.577(6), and 2.611(6) Å, respectively, and the angles of P1–Ag–P2, P1–Ag–P3, and P2–Ag–P3 are 112.0(2), 112.9(2), and 112.3(2)°, respectively, and the angles of S–Ag–P1, S–Ag–P2, and S–Ag–P3 are 92.8(2), 116.7(2), and 108.7(2)°, respectively.[7i] The molecular structure of **2** is also compared with a recently reported complex, $[Ag(SPh)(PPh_3)]_4$,[11b] which has a highly distorted chair structure in the solid state with Ag–Ag contacts of 3.1300(3) Å; 3- and 4-coordinate (excluding Ag–Ag interaction) silver(I) atoms are coordinated by two or three bridged SPh groups and one PPh_3 ligand (the Ag–S1, Ag–S2, and Ag–P1 distances are 2.5245(7), 2.5147(8), and 2.4500(7) Å, respectively; the Ag2–S1, Ag2···S2, Ag2–S2′, and Ag2–P2 distances are 2.4925(7), 3.0006(8), 2.5593(8), and 2.4213(7) Å, respectively).

On the other hand, a crystal-structure determination of **3** was attempted *at least* four times using different crystals, but there has remained a problem due to a disorder or fluxional behavior of the PPh_3 group in the crystals.[12] However, (1) the molecular structure of **3** with an AuSP core of almost linear coordination (Au–S and Au–P distances of 2.295(3) and 2.254(2) Å, respectively; S–Au–P angle of 175.08(9)°) and (2) in the crystal structure, a supramolecular arrangement, as shown in Fig. 3, comprising repeated hydrogen bonds between the protonated carboxyl group and the pyridine nitrogen atom (O···N distance of 2.66 Å), were confirmed. These facts reflect an explicit difference between the pyridine ring of H_2mna and the benzene ring of H_2mba on the crystal structure. As a matter of fact, **5** in the solid state has shown a dimeric structure via hydrogen-bonding interactions between the carboxyl groups (O2···O3^i distance 2.56(1) Å).[7i]

Behavior in $CHCl_3$ Solution and NMR (^{31}P, ^{109}Ag, ^1H, and ^{13}C). Solution molecular-weight measurements of **1** (Found: 621; Calcd: 786.6) and **2** (Found: 510; Calcd: 1048.9) in $CHCl_3$ indicate that these complexes are present as dissociation equilibrium species. Rapid dissociation equilibria of phosphine ligands in several silver(I)–phosphine complexes in organic media have generally been well-defined.[13] Since **1** and **2** are formed in the presence of excess amounts of PPh_3, it would be reasonable to postulate that the PPh_3 ligands from these complexes are successively dissociated in $CHCl_3$ solution. As a matter of fact, one of the coordinating PPh_3 ligands in **2** has a tendency to readily dissociate in solution, since the solution of **2** dissolved in CH_2Cl_2 gave crystals of **1** by vapor diffusion with an external solvent, diethyl ether (see the Experimental Section). Thus, if the successive dissociation of the PPh_3 ligands is this case, from the found and calculated molecular weights, a dissociation of **1** to $[Ag(Hmna)(PPh_3)]$ and free PPh_3 occurs with the degree of dissociation $\alpha = 0.267$, and that of **2** to $[Ag(Hmna)(PPh_3)_2]$, $[Ag(Hmna)(PPh_3)]$ and free PPh_3 occurs with $\alpha = 0.834$. Using these values, the distribution of the dissociation species of **2** is estimated to be 7.5% of $[Ag(Hmna)(PPh_3)_3]$, 34.2% of $[Ag(Hmna)(PPh_3)_2]$, 10.2% of $[Ag(Hmna)(PPh_3)]$ and 48.1% of free PPh_3, while that of **1** is found to be 57.8% of $[Ag(Hmna)(PPh_3)_2]$, 21.1% of $[Ag(Hmna)(PPh_3)]$ and 21.1% of free PPh_3. Thus, the molecular formulas and molecular structures of **1** and **2** are represented only in the solid state. This feature is in contrast to that of the related, "rigid" complex **4**, which has been shown to be present as a monomeric 4-coordinate geometry both in solution and in the solid state.[7i] On the other hand, a solution molecular-weight measurement of **3** (Found: 655; Calcd: 613.4) suggests that this complex in solution is present as an almost monomer.

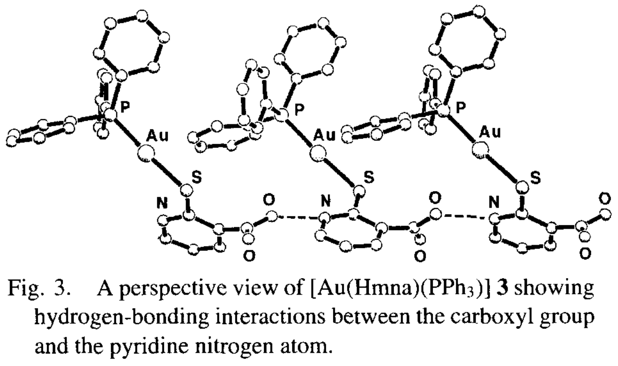

Fig. 3. A perspective view of $[Au(Hmna)(PPh_3)]$ **3** showing hydrogen-bonding interactions between the carboxyl group and the pyridine nitrogen atom.

No ^{31}P signal of the free PPh_3 (−5.33 ppm) ligand was observed in the ^{31}P NMR spectra of **1** and **2** at room temperature in $CDCl_3$. Also, the ^{31}P NMR spectra of **1** and **2** in the presence of extra 2 equiv of the free PPh_3 showed broad signals at −3.68 and 1.50 ppm, respectively, both being with a shoulder, and no ^{31}P signal due to the free PPh_3 in both solutions has been observed. Thus, the ^{31}P NMR single peaks observed at 6.48 ppm for **1** and at 3.27 ppm for **2** show only the averaged peaks resulting from a rapid dynamic exchange of the PPh_3 ligands. These signals are compared with that of the "rigid" complex **4** in $CDCl_3$ observed at 4.55 ppm at room temperature.[7i] On the other hand, the ^{31}P NMR of **3** shows a signal at 37.2 ppm in CD_2Cl_2 due to a monomeric complex; it can be compared with that of **5** in $CDCl_3$ observed at 37.56 ppm.[7i]

The ^{109}Ag NMR spectra in $CDCl_3$ measured at room temperature, observed as only one resonance at 1055 ppm for **1** and at 1105 ppm for **2**, also show as averaged peaks among unequivalent ^{109}Ag species. These ^{109}Ag resonances are compared with a single peak at 1196 ppm in $CDCl_3$ at room temperature for **4**,[7i] and also with those of the averaged single peak due to a rapid, dynamic exchange in $CDCl_3$ solution at room temperature: at 1186 ppm for $[Ag(im)(PPh_3)_3]$ (Him = imidazole),[7g] at 994 ppm for $[Ag(1,2,3\text{-triz})(PPh_3)_2]_n$ (Htriz = triazole), and at 925 ppm for $[Ag(1,2,4\text{-triz})(PPh_3)_2]_n$.[7h]

In ^1H and ^{13}C NMR spectra measured in $CDCl_3$ at room temperature of complexes **1**—**3**, three proton and six carbon resonances of the coordinating $Hmna^-$ ligand were completely assigned, as well as their chemical shifts, as shown in Table 1.

Antimicrobial Activities in Aqueous Media. The antimicrobial activities in aqueous media of **1**—**3**, together with those of the free ligand and of the related complexes **4** and **5**, are listed in Table 3, as estimated by the minimum inhibitory concentration (MIC; $\mu g\,mL^{-1}$). Antimicrobial tests of **4** and **5** were first examined here.

The antimicrobial activities of the free ligand and the two silver(I) complexes **1** and **2** were estimated as being > 1000 $\mu g\,mL^{-1}$ for bacteria, yeast and mold, and thus showed no activity.

Table 3. Antimicrobial Activities of the Free H_2mna Ligand and Complexes **1**—**5** Evaluated by MIC[a)]

	H_2mna	$[Ag(Hmna)(PPh_3)_2]$ **1**	$[Ag(Hmna)(PPh_3)_3]$ **2**	$[Au(Hmna)(PPh_3)]$ **3**	$[Ag(Hmba)(PPh_3)_3]$ **4**	$[Au(Hmba)(PPh_3)]$ **5**
Escherichia coli	>1000	>1000	>1000	>1000	1000	>1000
Bacillus subtilis	>1000	>1000	>1000	62.5	15.7	>1000
Staphylococcus aureus	>1000	>1000	>1000	62.5	31.3	>1000
Pseudomonas aeruginosa	>1000	>1000	>1000	>1000	1000	>1000
Candida albicans	>1000	>1000	>1000	>1000	>1000	>1000
Saccharomyces cerevisiae	>1000	>1000	>1000	>1000	>1000	>1000
Aspergillus niger	>1000	>1000	>1000	>1000	>1000	>1000
Penicillium citrinum	>1000	>1000	>1000	>1000	>1000	>1000

a) Minimum inhibitory concentration ($\mu g\,mL^{-1}$).

The silver(I) ion, itself, as aqueous $AgNO_3$, has shown remarkable activities (6 $\mu g\,mL^{-1}$) against Gram-negative bacteria (*E. coli*, *P. aeruginosa*), moderate activities (100 $\mu g\,mL^{-1}$) against Gram-positive bacteria (*B. subtilis*) and no activity (> 1600 $\mu g\,mL^{-1}$) against yeast and mold.[7c,7f] Although polymeric silver(I) complexes with nitrogen donor ligands, such as $[Ag(im)]_n$,[7f] $[Ag(1,2,3\text{-triz})]_n$,[7h] and $[Ag(1,2,4\text{-triz})]_n$,[7h] have shown effective antimicrobial activities, almost all of their triphenylphosphine derivatives, such as $[Ag(im)(PPh_3)_3]$, $[Ag(1,2,3\text{-triz})(PPh_3)_2]_n$, and $[Ag(1,2,4\text{-triz})(PPh_3)_2]_n$, have shown no activity (> 1000 $\mu g\,mL^{-1}$). This fact should be attributed to whether or not the complexes can possess a further ligand-replacement ability in aqueous media with the biological ligands, but not to their low solubility in water.[7f,7g,7h] In fact, all of the silver(I) complexes mentioned above are almost insoluble in water.

The precursor, $[Ag(Hmba)]_n$, has shown excellent activities (< 2 $\mu g\,mL^{-1}$) against Gram-negative bacteria, effective activities (16 $\mu g\,mL^{-1}$) against Gram-positive bacteria (*B. subtilis*, *S. aureus*) and moderate activities (125 $\mu g\,mL^{-1}$) against one yeast (*S. cerevisiae*),[7c] whereas **4** shows effective activities (16 and 32 $\mu g\,mL^{-1}$) only against Gram-positive bacteria (*B. subtilis* and *S. aeruginosa*, respectively). In general, the triphenylphosphine derivatives so far have shown narrow spectra of antimicrobial activities or poor activities. Thus, the lack of activity observed in **1** and **2**, as well as the narrow spectrum observed in **4**, is not a striking aspect. From the viewpoint of metal-based drug design, the lack of activity of the PPh_3 derivatives is also a crucial feature which can be utilized.

On the other hand, there have been only a few reports concerning antimicrobial activities by the gold(I) complexes.[5] In Table 3, it may be reasonable that **5** shows no activity. Of particular note is, however, the fact that **3** shows moderate activities (63 $\mu g\,mL^{-1}$) against two Gram-positive bacteria, since the gold(I) complexes with sulfur donor ligands and without a PPh_3 ligand, such as $\{Na_2[Au(tma)]\}_n$ (H_3tma = thiomalic acid) and $Na_3[Au(mba)_2]$, have shown no and poor activities against Gram-positive bacteria, respectively. Also, we have recently found that several gold(I) complexes with an AuNP (N = nitrogen-containing heterocycle, P = PPh_3) core have commonly shown effective and selective activities against only Gram-positive bacteria.[7l,7m] In relation to these facts, tetrahedral gold(I) complexes $[Au\{cis\text{-}Ph_2P(CH{=}CH)PPh_2\}_2]Cl$ and $[Au\{Ph_2P(CH_2)_3PPh_2\}_2]Cl$ with chelating diphosphine ligands have been reported by Berners-Price et al. to show modest activities against Gram-positive bacteria (*S. aureus*) and yeast (*C. albicans*), but no activity against Gram-negative bacteria (*E. coli* and *P. aeruginosa*).[5b] These activities have been tested in DMSO solution. The reported results are consistent with ours tested in a suspension of aqueous media. At present, we can present no reasonable interpretation of these facts. However, it is likely that the antimicrobial mechanism and mode of action of gold(I) complexes are different from those of the silver(I) complexes.

Conclusion

Using a polyfunctional mercaptonicotinic acid (H_2mna), in the presence of PPh_3 ligand, two novel silver(I) complexes, **1** and **2**, and one novel gold(I) complex **3** were isolated in good yields (72.8, 55.2, 63.0%, respectively). Several different points from the previous silver(I) and gold(I) complexes with the related ligand, 2-mercaptobenzoic acid (H_2mba), have been found. (1) The synthetic reactions of **1** and **2** require excess amounts of the PPh_3 ligand to the cluster precursor $[Ag(Hmna)]_n$, i.e., three-times excess of PPh_3 for **1** and twenty-times excess of PPh_3 for **2**. One reason for this requirement has been attributed to the Ag–N bonds present in the precursor, and also to an intramolecular Ag–N interaction present in **1**. These facts are in contrast to a stoichiometric formation of **4**. (2) X-ray crystallography has revealed that **1** and **2** were discrete monomers in the solid state. The coordination geometry of **1** was a trigonal pyramid with an $AgSP_2$ core, and there was an intramolecular weak interaction between the silver(I) center and the aromatic nitrogen atom, while that of **2** was a distorted tetrahedron with an $AgSP_3$ core. The crystal-structure determination of **3** has a problem, because of a disorder or fluxional behavior of the PPh_3 group. However, its supramolecular arrangement in the solid state through a hydrogen-bonding interaction between the carboxyl group and the aromatic nitrogen atom was confirmed. Such interactions were also supported by FT-IR measurements. The supramolecular feature of **3** is in contrast to the dimeric structure of **5** with hydrogen-bonding interactions between the carboxyl groups. (3) In $CHCl_3$ solution, both **1** and **2** were under rapid, dissociation equilibrium of PPh_3 ligands, whereas **3** was not. Both complexes **2** and **4** have an $AgSP_3$ core in the solid state, but their behaviors in $CHCl_3$ solution were quite different. (4) In an antimicrobial test in an aqueous suspension of **1**—**5**, selective and moderate activities by **3** and **4** against two Gram-positive bacteria were observed. The title complexes are also of interest as a possible new type of coinage metal-based drugs; studies of other biological activities are planned.

Experimental

Materials. All chemicals were of reagent grade and were used as received: $(C_2H_5)_4NCl$, 2-mercaptonicotinic acid (H_2mna), $AgNO_3$, $Na[AuCl_4]\cdot 2H_2O$, NaOH, 1.0 M aqueous HNO_3 (1 M = 1 mol dm^{-3}), 1.0 M aqueous NaOH, triphenylphosphine (PPh_3), acetonitrile, ethanol, methanol, chloroform, dichloromethane, acetone, diethyl ether (all from Wako); CD_2Cl_2, $CDCl_3$, DMSO-d_6, (Isotec). $[AgCl(PPh_3)_3]$[14] and $[AuCl(PPh_3)]$[15] were prepared according to the literature, respectively.

Instrumentation/Analytical Procedures. Complete elemental analyses after overnight drying under 10^{-4}—10^{-3} Torr (1 Torr = 133.322 Pa) were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). CHNS analyses were performed using a Perkin–Elmer PE2400 series II CHNS/O Analyzer. Infrared spectra were obtained on a Nicolet 510 FT-IR spectrometer as KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG 8101D and TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of 4 °C min^{-1} between 20 and 500 °C.

Molecular-weight measurements in solution based on the vaporimetric method using a vapor-pressure osmometer were performed by Mikroanalytishes Labor Pascher (Remagen, Germany) and evaluated for 14.68 mg of complex **1** dissolved in 1.1947 g of chloroform, 18.56 mg of complex **2** dissolved in 1.0536 g of chloroform, and 21.80 mg of the complex **3** dissolved in 2.4772 g of chloroform.

^1H NMR (399.65 MHz), $^{13}C\{^1H\}$ NMR (100.40 MHz), and $^{31}P\{^1H\}$ NMR (161.70 MHz) spectra in solution were recorded at 23 °C in 5 mm outer-diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data-processing system. Proton and $^{13}C\{^1H\}$ NMR spectra of the complexes were measured in $CDCl_3$ or CD_2Cl_2 solution with reference to an internal-standard $SiMe_4$. The chemical shifts are reported on the δ scale and resonances downfield of $SiMe_4$ ($\delta = 0$) are recorded as positive. $^{31}P\{^1H\}$ NMR spectra were measured in $CDCl_3$ or CD_2Cl_2 solution with reference to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. The chemical shifts are reported as negative for resonances upfield of H_3PO_4 ($\delta = 0$).

The ^{109}Ag NMR (18.45 MHz) were recorded at 23 °C in 10 mm outer-diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe. The ^{109}Ag NMR spectra of the complexes were measured in $CDCl_3$ solution with reference to an external standard of saturated $AgNO_3$–D_2O solution by a substitution method. The chemical shifts were recorded as positive for resonances downfield of $AgNO_3$ ($\delta = 0$). Spectral parameters for ^{109}Ag NMR include: pulse width 13.2 μs; acquisition time 0.390 s; recycle time 1.39 s; sweep width 21008 Hz.

Antimicrobial Activities. The antimicrobial activities of the silver(I) and gold(I) compounds prepared here were estimated based on the minimum inhibitory concentration (MIC: μg mL^{-1}) as usual.[7a,7c,7f,7h]

Bacteria were inoculated into 5 mL of liquid medium (SCD medium) and cultured for 24 h at 35 °C. Yeast were inoculated into 5 mL of liquid medium (GP medium) and cultured for 48 h at 30 °C. The cultured fluids were diluted, adjusted to a concentration of 10^6—10^7 mL^{-1} and used for inoculation in the MIC test. As for the mold culture, the agar slant (PD agar medium) for one week cultivation at 27 °C was gently washed with saline containing 0.05% Tween 80. An obtained spore suspension was adjusted to a concentration of 10^6 mL^{-1} and used for inoculation in the MIC test.

Test materials **1**—**5** and the free ligand were suspended in water. Such suspensions were then diluted with SCD medium for bacteria and with GP medium for yeast and mold. Using them, two-fold diluted solutions with concentrations of 1000 μg mL^{-1} to 2 μg mL^{-1} were prepared. Each 1 mL of culture medium containing various concentrations of test materials was inoculated with 0.1 mL of the microorganism suspension prepared as mentioned above.

Bacteria were cultured for 24 h at 35 °C, yeast for 48 h at 30 °C, and mold for one week at 25 °C; then the growth of microorganisms was observed. When no growth of microorganisms was observed in the medium containing the lowest concentration of test materials, the MIC of the test material was defined at this point of dilution.

SCD, GP, and PD media were purchased from Nissui.

Preparation of Water-Insoluble, Polymeric Precursor $[Ag(Hmna)]_n$. To a clear, yellow solution of 0.78 g (5.00 mmol) of H_2mna ligand dissolved in 10 mL of 1 M aqueous NaOH solution (10.00 mmol) was dropwise added a stirred, clear solution of 0.85 g (5.00 mmol) of $AgNO_3$ in 5 mL water. Although a white precipitate formed initially, a clear yellow solution was obtained during stirring. To the clear yellow filtrate passed through a folded filter paper (Whatman No. 5) was dropwise added 10 mL of 1 M HNO_3 aqueous solution and a solution was stirred for 1 h. The yellow precipitate formed was collected on membrane filter paper (JG 0.2 μm), then was washed with (100 mL×3) water, (50 mL×3) ethanol, and (100 mL×3) acetone, and finally with (50 mL×3) ether and dried in vacuo. The yellow powder obtained was dispersed in 20 mL water. To it was added 10 mL of a 1 M aqueous NaOH solution, followed by passing through a folded filter paper (Whatman No. 5). A clear yellow filtrate was added to 150 mL of ethanol. The yellow-white precipitate was collected on a membrane filter (JG 0.2 μm) and washed with (50 mL×3) ethanol, (100 mL×3) acetone, and (100 mL×3) ether, and dried in vacuo. This reprecipitation was repeated again. A light-stable yellow powdery solid obtained in 0.93 g yield (71.0% based on an assumed formula of $[Ag(Hmna)]_n$) was sparingly soluble in DMSO, insoluble in water, ethanol, methanol, acetone, and ether, but soluble only in aqueous NaOH solution to give a yellow solution.

When an $AgNO_3$ and 1 M HNO_3 aqueous solution as starting material was used for the preparation, the final compound was sometimes contaminated with NO_3^- ion. To avoid any contamination by NO_3^- ion, Ag_2O and sulfuric acid can be used with almost the same yields and higher purity of $[Ag(Hmna)]_n$ maintained.[7k]

$[Ag(Hmna)(PPh_3)_2]$ 1 from Polymeric Precursor $[Ag(Hmna)]_n$. To a yellow suspension of 0.262 g (1.00 mmol) of powdery solid $[Ag(Hmna)]_n$ in 60 mL ethanol was added a clear colorless solution of 0.787 g (3.00 mmol) of PPh_3 in 20 mL dichloromethane. Stirring continued until the solution became clear yellow. The clear filtrate obtained by passing through a folded filter paper (Whatman No.5) was slowly evaporated at room temperature. After three days, yellow plate crystals formed, which were collected on a membrane filter (JG 0.2 μm), then washed with water (100 mL), ethanol (200 mL×2) and diethyl ether (100 mL), and dried in vacuo for 2 h. The yellow plate crystals were obtained in 0.534 g (67.9%) yield as the first crop and then in 0.039 g (5.0%) yield as the second crop; the combined yield was 0.573 g (72.8%). The compound as **1** was light- and thermally stable, and soluble in chloroform and dichloromethane, but insoluble in ethanol, methanol, water and diethyl ether.

Compounds obtained by similar work-ups in the 1 : 1 and 1 : 2 molar ratio reactions of $[Ag(Hmna)]_n$ and PPh_3 were a mixture of **1** and unreacted $[Ag(Hmna)]_n$; therefore, the yield of **1**, itself, was low.

$[Ag(Hmna)(PPh_3)_2]$ 1 from Precursor $[AgCl(PPh_3)_3]$. To a yellow suspension of 0.155 g (1.00 mmol) of H_2mna in 50 mL ethanol was added 0.040 g (1.00 mmol) NaOH dissolved in 10 mL ethanol, followed by stirring for 30 min. The obtained clear-yellow solution was added dropwise to 0.930 g (1.00 mmol) $[AgCl(PPh_3)_3]$ dissolved in 20 mL dichloromethane, followed by stirring 1 h. The yellow suspension was filtered through a folded filter paper (Whatman No.5). The clear-yellow filtrate was slowly evaporated at room temperature. Yellow plate crystals formed which were collected on a membrane filter (JG 0.2 μm), washed with water (100 mL), then ethanol (150 mL) and finally with diethyl ether (100 mL), and dried in vacuo for 2 h. Light- and thermally-stable, yellow plate crystals obtained in 0.447 g (56.8%) yield were soluble in chloroform and dichloromethane, but insoluble in ethanol, methanol, water and diethyl ether.

$[Ag(Hmna)(PPh_3)_3]$ 2. To a yellow suspension of 0.262 g (1.00 mmol) of powdery solid $[Ag(Hmna)]_n$ in 10 mL dichloromethane was added a clear colorless solution of 5.24 g (20.00 mmol) of PPh_3 in 20 mL dichloromethane, followed by stirring for 1 h. The clear yellow filtrate obtained by passing through a folded filter paper (Whatman No.4) was placed in an internal, small open vial, and diethyl ether was used as an external solvent within a screw-capped larger vial for vapor diffusion. After one week at room temperature, pale-yellow plate crystals formed, which were then collected on a membrane filter (JG 0.2 μm), washed twice with 100 mL diethyl ether, and dried in vacuo for 2 h. The yield was 0.58 g (55.2%). Relatively light- and thermally-stable, yellow plate crystals obtained as compound **2** were soluble in chloroform and dichloromethane, but insoluble in water and diethyl ether.

The reaction of 1 : 10 molar ratio of $[Ag(Hmna)]_n$: PPh_3 also gave the same compound **2**, but with a lower yield, i.e., in 0.37 g (35.0%) yield. On the other hand, the reaction of 1 : 5 molar ratio gave complex **1** in 0.22 g (27.9%) yield and none of complex **2**.

The vapor diffusion in a solution system consisting of e.g., 1.0 g of **2** dissolved in 6.5 mL CH_2Cl_2 as the internal solution and 30 mL diethyl ether as the external solvent, gave crystals of **1** in 0.25 g yield. Thus, one of the coordinating PPh_3 ligands in **2** has a tendency to dissociate in solution.

$[Au(Hmna)(PPh_3)]$ 3. To a yellow solution of 0.155 g (1.00 mmol) of H_2mna and 0.495 g (1.00 mmol) of $[AuCl(PPh_3)]$ dissolved in 80 mL acetone was added 1 mL (1.00 mmol) of 1.0 M aqueous NaOH, followed by stirring the yellow-white suspension for 30 min. NaCl formed was filtered off through a folded filter paper (Whatman No.2). The obtained clear-yellow solution was concentrated to ca 10 mL by a rotary evaporator at 50 °C. The solution was added dropwise to 100 mL of water, and the formed yellow powdery solid was collected on a membrane filter (JG 0.2 μm), washed with water (50 mL×2), then diethyl ether (50 mL×2), and dried in vacuo for 2 h. The yellow powdery solid was dissolved in 10 mL dichloromethane, followed by passing through a folded filter paper (Whatman No.2). The pale-yellow filtrate was used as an internal solution and diethyl ether was used as an external solvent for vapor diffusion at room temperature. After 1 day, colorless needle crystals began to form. After a few days, the crystals were collected on a membrane filter (JG 0.2 μm), washed with diethyl ether (100 mL×2), and dried in vacuo for 2 h. Light- and thermally-stable, colorless needle crystals obtained in 0.39 g (63.0%) yield were soluble in acetone, DMSO, chloroform and dichloromethane, but insoluble in water and diethyl ether.

X-Ray Crystallography. Each single crystal of **1** and **2** was mounted on a glass fiber and used for measurements at room temperature of precise cell constants and intensity data collection on a

Table 4. Summary of Crystal Data for Complexes **1** and **2**

	1	**2**
Formula	$C_{42}H_{34}NO_2P_2SAg$	$C_{60}H_{49}NO_2P_3SAg$
Formula weight	786.61	1048.90
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a/Å	13.142(3)	13.22(4)
b/Å	13.362(7)	28.370(4)
c/Å	10.85(2)	13.985(6)
α/°	101.23(8)	90
β/°	98.23(5)	92.5(1)
γ/°	82.63(3)	90
V/Å^3	1839(3)	5238(14)
d_{calcd}/g cm^{-3}	1.42	1.33
Z	2	4
μ/cm^{-1} (Mo$K\alpha$: λ=0.7107 Å)	7.27	5.50
No. of total reflections	8886	12509
No. of unique reflections	8441	12004
No. of observed reflections	6607 ($I>2.0\sigma(I)$)	5341 ($I>2.0\sigma(I)$)
R[a)]	0.029	0.067
R_w[b)]	0.093	0.135

a) $R=\sum(|F_o|-|F_c|)/\sum|F_o|$, b) $R_w=[\sum\omega(|F_o|-|F_c|)^2/\sum\omega(|F_o|^2)]^{1/2}$.

Rigaku AFC5S diffractometer. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections based on a PSI scan were applied to the data of **1** and **2**. The overall averaged transmission factors of **1** and **2** were in the range 0.846—1.000 and 0.735—0.983, respectively. The structures were solved by direct methods followed by a subsequent difference Fourier calculation and refined by a full-matrix least-squares procedure using the TEXSAN package.[16]

For **1**, non-hydrogen atoms were refined anisotropically; one hydrogen atom was located in the calculated position and other hydrogen atoms were refined isotropically. For **2**, all atoms, except for hydrogen, were refined anisotropically and hydrogen atoms were located in the calculated positions ($d_{\mathrm{C-H}} = 0.95$ Å). The residual peaks in the final difference Fourier map corresponded to less than 0.5 e Å^{-3}, except for the neighborhood of the Ag atom. Crystal data, data collection and the refinement for **1** and **2** are summarized in Table 4.

The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and temperature factors of hydrogen atoms, and the $F_o - F_c$ tables are deposited as Document No. 73024 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC139841/139842.

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$V = 2289.5(6)$ Å^3, space group $P2_1/c$ (No. 14), $Z = 4$, $F(000) = 1184$, Mo $K\alpha$ radiation, room temperature. $D_{\mathrm{cal}} = 1.779$ g cm^{-3}. $\mu = 66.29$ cm^{-1}. A colorless needle crystal of **3** ($0.4 \times 0.1 \times 0.1$ mm^3) was mounted on glass fiber and transferred to a Rigaku AFC5S diffractometer. The structure was solved by direct method and refined by full-matrix least-squares using TEXSAN software package.[16] The R and R_w factors after refinement using 3232 observed reflections ($I > 2\sigma(I)$) among 5453 unique reflections were 0.042 and 0.034, respectively. Non-hydrogen atoms were refined with anisotropic thermal factors. Hydrogen atoms were refined with isotropic temperature factor. Disorder was found in one of three phenyl rings and the temperature factor of the carbon atoms was too much large.

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